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INVESTIGATIONS OF RED SOILS OF ATTICA, GREECE

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The soils of the region adjacent to the Mediterranean recently have become the subject of systematic studies. The interesting works of Del Villar (4), Blanck (2) and his collaborators, Reifenberg (8, 28) Harassowitz (14, 15) and a number of other eminent investigators are proof of the importance of such studies. Practically all these authors have the same point of view as that advanced by Neumayer (23), namely, that the typical Mediterranean red soils ("terra rossa") are formed on limestone. Fuchs (9), about the same time, supported this view more definitely, asserting that typical red soils ("terra rossa") are laid only on pure and hard white limestone and never on soft marnish or chalk-like ones.

It is universally admitted that typical red soils are always found on a lime parent rock. Zvorykin (39) states that under the climatic conditions of Middle Europe, in Moravian Karst, where Devonian limestone is very common, we have red clay which serves as parent rock for the development of podzolic soils, which are formed by the washing out of $CaCO_3$ and the replacement of exchangeable bases from the parent rock. Jahn (16) in his geological sketch calls this type of red clay "terra rossa."

Under Greek conditions, at moderate altitudes, soft limestones generally do not develop typical red soils, but we have soils of the rendzina type varying in color from gray to dark gray. In this respect our results agree with those of Fuchs (9) and Glinka.

On the hillsides of Thessalia, however, in the vicinity of the city of Larissa, the rendzina type of soils under the influence of sheet erosion formed reddish brown soils with granular structure. These soils are more thoroughly saturated with the bivalent cations Ca and Mg than are the typical red soils. In this region we find a decidedly complicated type of soils, which are influenced by the topographic conditions. We encounter surfaces that are entirely washed off from the parent rock, which thus remains exposed; surfaces occupied by rendzina soils; and, lastly, surfaces with strips of reddish brown soils.

We are of the opinion that, under the conditions mentioned, a partial application of the theory of Stremme (36) as to the origin of red or reddish brown soils under the influence of erosion can be made. Robinson (29) is quite right, however, in stating that Stremme's theory cannot be applied to the entire Mediterranean region.

Although it is well known that red soils are formed on rocks that contain large quantities of $CaCO_3$, we have observed in our studies of soil profiles from Thessalia, near the village of Tsagezi, on riparian terraces composed of weathered carbonate-free schists, a pale reddish tint on the main ocher ground. On the upper horizon we noticed very distinct red spots as well as narrow red veins, the latter being spread over all the profile to a depth of 105 cm. Lower horizons than these could not be obtained with ordinary tools.

During the last four years, while visiting practically all of Thessalia, Macedonia, and Attica, we made field observations and collected many monoliths for laboratory study. On the basis of these observations and laboratory investigations, the latter not being quite completed, we propose that reddish soil formations are found throughout these regions, the differences within the soils varying with the different parent rocks and with the topography.

In 1924, while working as an investigator at the Pedological Laboratory of Brünn, the junior author made several excursions in Moravia with Professor Afanasiev, who drew attention to the presence in the author's monoliths of pale reddish hues in horizon A_2 of certain podzolic soils which were developed on carbonate-free parent rocks. On these grounds Afanasiev advanced a theory that the red soil formation throughout all Middle Europe is just beginning. In any event this question deserves a wider and more systematic study.

In some regions, in Thessalia and especially in Macedonia, the red soils are subjected to the saline process and, under the influence of more or less advanced saturation with Na, are gradually changing their morphology, becoming darker in color, especially in the B horizons, and are forming hardpan. For the most part, however, it is possible to recognize that we have before us a transformed red soil. Glinka (12, p. 414), who has observed red soils in the neighborhood of Salamanka, Spain, also speaks of the existence of saline and non-saline red soils. Del Villar (5) states, too, that in red soils there is a considerable quantity of absorbed Na. In Macedonia the influence of Na is very pronounced, especially in carbonate-free red soils. Having already undergone a degradation process, the saline red soils of Greece contain, for the most part, no adsorbed Na. In the laboratory one can discover only traces of the influence of this cation.

This phenomenon could be explained, according to investigations of Zvorykin and Katakosinos[1] and of Zvorykin (40), by the lowering of the base level of erosion, which is closely connected with the lowering of the ground water level. This question is thoroughly treated by Polynov (27) in his investigation of the Don Valley, Russia.

The greatest transformations of the soils of Greece, particularly of Attica, are due to the influence of sheet and gully erosion. Periodical winter floods, caused by the very uneven distribution of rainy seasons and by the topography,

[1] Zvorykin, I., and Katakosinos. Considerations générales sur la salinité des terres dans la plaine de Salonique. Unpublished.

destroy the soil and transport it to lower spots. In this manner the main type of a new soil originates.

The action of erosion must be attributed to the fact that in regions of typical red soils we very often find yellow and even gray soils. In studying the morphology of the profiles, not taking into account the physico-geographical conditions, we can find inside the boundaries of small regions a mixture of soil types belonging to different zones, as is shown by the map of Stremme (37, p. 18). In the vicinity of Salonica, in Macedonia, the same author shows brown and forest soils, instead of white and black alkali soils, and degraded black alkali soils formed on red soils.

On the basis of the study of the action of erosion, red soils may be divided into two groups as follows: first, soils formed *in situ* on a stable topography, and secondly, transported soils deposited on a topography still in the process of formation. The latter are sometimes very deep and consist of buried horizons of red soils alternating with stony deposits, the pebbles of which may be smooth or rough according to the character of their origin, alluvial, deluvial, or proluvial,[2] as explained by Pavlov (25, 26). Similar erosion processes undoubtedly change the mechanical and the chemical composition of the red soils, as discussed by Agafonov (1) in his investigation of the red soil of Brazil.

On the basis of the foregoing facts, in order to form an idea of the red soils of Greece it seems necessary first to study soils located in a stable topographic position, where the process of new formation has had time to manifest itself on the maturity of the soil profile. Only under such conditions can we speak of the age of the soil, because, as Sokolov (33) points out, the age of the soil does not depend directly on the age of the parent rock, but rather on the final stages of the orographic elements, at which point the geological processes are substituted by soil formation.

Having on hand these experimental data, we chose Attica as a typical province for the study of red soils.

To characterize Attica, from the climatic point of view, we have used the records for the last 50 years of the Meteorological Observatory of Athens, such as temperature, quantity of rainfall, and relative moisture, published by Eginitis (6), and also the evaporation records of Findiklis (7) for the period 1894–1928. The evaporation records were obtained by means of a Pich evaporimeter. Findiklis remarks that these figures may be somewhat high, but for our work such observations are of marked interest even though they are only of a comparative nature. The results of these observations are shown in table 1.

From the table it is evident that the rainfall for the entire year is divided into two periods: the wet winter period and the dry summer one. With the wet period correspond the lowest temperature of the air and the highest relative

[2] The terms "deluvial" and "proluvial" were introduced by Pavlov, the latter to designate the unsifted deposits formed at the estuaries of mountain valleys. These deposits are products of sudden floods.

TABLE 1

Climatic records for Attica, 1853–1928

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER	TOTAL OR AVERAGE
Rainfall, 1858–1928*.....*mm.*	52.14	39.37	36.10	19.51	20.91	13.75	6.34	8.66	13.38	41.25	71.84	66.64	392.83
Temperature, 1853–1903†.....°C.	8.77	9.58	12.21	15.85	20.78	25.17	28.06	27.63	24.17	19.80	14.42	10.69	18.14
Relative moisture, 1860–1903.....*per cent*	72.4	71.1	67.1	62.7	58.2	53.6	46.0	45.5	53.8	65.2	72.1	73.7	61.4
Evaporation, 1894–1928‡.....*mm.*	65.81	67.39	90.97	116.94	155.13	196.48	251.02	235.55	178.39	112.86	78.40	64.69	1,613.73

* After Eginitis (6) and Findiklis (7).
† After Eginitis (6).
‡ After Findiklis (7).

TABLE 2

Chemical analysis of soil profiles 3 and 4

ATTICA	HORIZONS	H_2O AT 105°C.	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	CO_2	LOSS OF ORGANIC MATTER ON IGNITION	TOTAL
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Profile of Agios Andreas	0–10	2.19	41.85	8.18	5.24	0.31	20.38	1.23	1.20	0.93	0.15	0.01	14.49	5.92	99.89
	10–32	1.75	23.92	6.95	3.04	0.26	34.32	0.89	0.87	0.68	0.26	0.01	25.67	3.03	99.90
	32–60	1.30	24.49	6.89	2.99	0.09	35.39	0.81	0.89	0.63	0.11	trace	25.19	2.47	99.95
	60–120	2.77	28.37	7.78	4.54	0.07	31.62	0.89	0.94	0.68	0.16	0.02	22.35	2.50	99.92
Profile of Halandri	0–27	1.84	59.40	10.84	5.62	0.15	10.02	1.21	1.31	0.87	0.12	0.03	6.15	4.47	100.09
	27–43	2.12	60.98	11.73	5.80	0.15	7.82	0.79	0.97	1.16	0.16	0.02	5.27	5.08	99.93
	43–55	2.36	52.89	11.62	5.16	0.18	13.82	0.76	1.35	0.48	0.19	trace	8.91	4.53	99.89
	55–85	1.83	51.54	9.81	4.65	0.13	16.83	1.22	1.09	0.79	0.19	trace	10.95	3.12	100.32
	85–120	1.16	48.10	8.64	3.90	0.14	20.09	0.95	1.21	0.46	0.19	trace	13.17	3.19	99.94

moisture. The average temperature in the coolest month of January is above 0°C.

Kappen (17), on the basis of meteorological records, classifies the climate of Attica as warm with a dry summer. De Martonne (21) characterizes the climate of all Greece as Mediterranean-Continental with a mild and wet winter period followed by a dry summer, during which the conditions become similar to those of a desert.

Findiklis (7), comparing the evaporation records of Athens with those obtained in a near-by desert, such as Turkestan, Sudan, or Egypt, concludes that they are very similar. If the classification of MacDougal (20) is followed, the climate of Attica during the dry period and at a moderate altitude can be classified as that of a desert. Such conclusions seem to be more justified as the average annual rainfall for Greece, as a rule, is not great and, furthermore, during the summer months it drops to a minimum.

We are of the opinion that the occurrence of two sharply defined periods of rainfall is of great significance for the various soil forming processes; for example, during the rainy period the soils become saturated to a considerable depth and remain in this state from November until May, when the soil begins to dry.

It seems possible that the soils of Greece undergo, during the year, two periodical influences; namely, first, the eluviation, during the wet period, at which time the soil solution descends; and secondly, the illuviation, during the dry period, at which time the soil solution ascends. The presence of colloids complicates the situation. If the colloids are reversible, as in the case of soils saturated with Na, then under Greek conditions in the absence of periodic or continuous uplifting of the ground water, the formation of solodi from the black alkali soils follows.[3] Under such conditions we have a sharp differentiation of the profile into horizons, alteration of the structure, and a speedy decomposition of the colloidal part of the soil, especially in the upper horizon.

Reifenberg (8, 28) was the first to study soils that contain irreversible and mutually coagulating colloids. We are of the opinion that the red soils of the Mediterranean region are very appropriate material for such study.

STUDY OF SOIL PROFILES

We know very definitely that color and the conditions of the deposition of "terra rossa" are constant at different altitudes, as stated by Robinson (29) and by Zvorykin (39), but the soils formed on it have different characters depending on the physico-geographic characteristics of the country, which in turn determine the maturity of the soil profile. This is substantiated by chemical analyses.

From our monolith collection, we selected profiles 3 and 4 for this study.

Monolith 3 (plate 1, fig. 1) was taken on December 14, 1935, along the main road from Athens to Marathon, in Attica, 2 km. south of the chapel of

[3] See footnote 1.

Agios Andreas on the ridge of a terrace elevated 40–45 m. above sea level and abruptly sloping down to a beach. The ridge of the terrace under the influence of gully erosion is cut by a deep ravine having steep slopes. The terrace is composed of limestone rocks weathering sometimes to a considerable depth. Groves of pine trees (*Pinus halepensis*) alternate with strips of ploughed fields. The mountains overlooking the terrace are composed of hard white and grayish white limestones.

Description of profile 3

Horizon I, 0–10 cm. The surface is covered with a very thin (0.5 cm.) broken layer of decomposing pine needles. The horizon is moist; light red with a yellowish tint and with a gray stain of humus; structureless, having in the lower part small quantities of lime concretions of ovoid form; very loose (plate 2, fig. 1); and fragile. This horizon is very rich in $CaCO_3$.

Horizon II, 10–32 cm. This horizon is moist, pale reddish, soft, loose, and structureless. It contains a large quantity of soft ovoid concretions with a yellowish bloom and also some lumps of limestone (plate 2, fig. 2), roughened by the process of weathering and representing the remnants of the original parent material. The hardened nuclei of these remnants are covered with tuff. This horizon is very rich in $CaCO_3$.

Horizon III, 32–60 cm. This horizon is slightly moist, more compact than the former and lighter, and the reddish straw colored soil is pierced with limy veins and concretions as described for horizon II. Often we encounter rough remnants of hard limestone. This horizon is very rich in $CaCO_3$.

Horizon IV, 60–120 cm. This horizon is slightly moist and very hard with its reddish background permeated by lime veins, bands, and spots. A large number of concretions and remnants of tuff-covered lime are encountered. It is very rich in $CaCO_3$.

The process of soil formation and the character of the topography of the land disclose a prolonged and deep weathering of the limestone deposits, which have been converted for a considerable depth into a loose mass, containing secondary products of weathering in the form of lime concretions, leaving behind only rough pieces of parent rock with a hard crust on one side. Profile 3 can be taken as an example of the process of red soil formation under forest conditions.

Monolith 4 (plate 1, fig. 2) was taken on December 15, 1935, near the village of Halandri, Attica, at a height of 215 m. above sea level on a flat and broad ridge of a terrace rising above the bank of the river Kifissos.

The ridge of the terrace is cut through by a gully erosion, which forms crevices with vertical sides occupying a limited portion of the ridge of the terrace. The inclination of the land, in sheet erosion, is comparatively slight, and the erosion cannot cause great change in the character of the soil.

Besides erosion, another factor contributes to the alteration of the soil hori-

zon. For many years these soils have been planted to vegetable crops and vineyards. As a result, the ground has been tilled very deep; therefore, we may consider the first two horizons (the second at least in its upper part) as thoroughly mixed and consequently as not having maintained their original material, which is the case for the most of the arable soils of Attica.

It is interesting to note that under the conditions of Attica fruit trees as well as olives at a certain age suffer from drought; often the tops (foliage and branches) of trees are dried up. This phenomenon might be explained on the basis of the physical structure of the lower horizons of the soil as described in the following section.

Description of profile 4

Horizon I, 0–27 cm. The surface is dark red, covered with a thin (0.5 cm.) blanket of turf, is structureless, becomes loose when dried up, contains a good many roots, and is very rich in $CaCO_3$.

Horizon II, 27–43 cm. This horizon is moist, dark red, slightly brighter than the foregoing, and has preserved the fine granular structure especially in the lower portion, notwithstanding cultivation. It is permeated with fine thin roots. In the dry state it is loose and dusty. It also contains large quantities of $CaCO_3$.

Horizon III, 43–55 cm. This horizon is moist and dark red but somewhat lighter than the preceding and much more compact, with thin lime veins resembling micellium and with a few white lime spots. In it we encounter scanty wilting roots and insect borings. This horizon is also rich in $CaCO_3$ content.

Horizon IV, 55–85 cm. This horizon is moist, brick-red colored with a pale ocher tint and lighter than the preceding, extremely compact, permeated by thin vertical flaws, and somewhat porous. It has white spots and small lime concretions as thin veins. It contains a small quantity of decaying roots and much $CaCO_3$.

Horizon V, 85–120 cm. This horizon is slightly moist, light reddish with a straw tint, entirely pierced by thin veins of lime, porous, extremely hard and compact even in its slightly moist state. It frequently occurs in the form of a lime hardpan. Occasional small dried out roots enriched with $CaCO_3$ are found.

The soil described has a mature profile where the processes of soil formation are very pronounced. Accumulations of lime occur in the compact low horizons. This compactness attains its maximum in the lower horizon, which becomes impervious to the root system. This accounts, we believe, for the drying of the tops of the fruit trees, a phenomenon analogous to that which goes on in solonetz or solonetz-like soils. The hardened horizon affects the roots in the manner described, notwithstanding the fact that it contains neither Na_2CO_3 nor sodium. This soil is very typical of the wide and open valleys of Attica.

Interpretation of chemical analyses

In studying the chemical properties of the respective horizons of the profiles total analyses were made, the exchangeable bases were determined by the Shmuk (30) method, and the Gedroiz (11, p. 282–287) 5 per cent KOH extraction method was applied. We also deemed necessary the determination of the hydrogen-ion concentration (pH), which we carried out electrometrically. The Gedroiz method was used for the determination of the degree of decomposition of the colloidal part of the soil. In our case we have considered indispensable the application of this method of Gedroiz because of the presence of hardpan in profile 4. Such hardpans are commonly formed on black alkali soils. In this particular case the tops of the fruit trees were dried up, which led us to believe that the soils under investigation were probably saturated with sodium.

TABLE 3

Chemical analyses of soil profiles 3 and 4 calculated on mineral content minus humus and CO_2 content

ATTICA	HORIZONS	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Profile of Agios Andreas	0–10	52.65	10.28	6.57	0.39	25.04	1.53	1.50	1.17	0.19	0.01
	10–32	33.59	9.75	4.27	0.36	48.20	1.25	1.21	0.95	0.36	0.01
	32–60	34.09	9.51	4.05	0.12	48.93	1.11	1.22	0.86	0.15	trace
	60–120	29.75	10.35	5.76	0.09	42.07	1.18	1.24	0.89	0.21	0.02
Profile of Halandri	0–27	66.46	12.13	6.28	0.16	12.39	1.34	1.46	0.96	0.13	0.03
	27–43	68.01	13.07	6.46	0.16	8.75	0.87	1.08	1.29	0.18	0.02
	43–55	61.09	13.42	5.94	0.21	15.96	0.87	1.56	0.55	0.22	trace
	55–85	59.98	11.42	5.04	0.14	19.58	1.41	1.26	0.91	0.28	trace
	85–120	56.84	10.21	4.61	0.16	23.20	1.12	1.43	0.53	0.21	trace

The results of our chemical investigations are shown in tables 2 and 3. The results in table 3 are calculated on mineral substances of the soil, minus the humus and CO_2 content. These tables indicate that the organic matter of the soils under investigation diminishes with the increase in depth and that this decrease is more pronounced in profile 3 (Agios Andreas) than in profile 4. The largest quantities of SiO_2 are found in the first horizon of profile 3 and in the first two horizons of profile 4. The SiO_2 decreases in the lower parts of the profile, particularly in profile 3.

The R_2O_3 accumulates in the surface horizons, the Fe_2O_3 more so than the Al_2O_3.

On the other hand the $CaCO_3$ in general increases with depth. It is interesting to note that the quantity of $CaCO_3$, as a general rule, is very large in the horizons of profile 3 and is greater even than that of SiO_2, notwithstanding the fact that the secondary lime formations, have, in the preparation of the sample, been sifted out by a 2-mm. sieve.

MgO is fairly evenly distributed among the horizons of profile 3, but in profile 4 it decreases somewhat in horizons II and III and again increases in horizons IV and V.

It is interesting to note that the K_2O content is, for the most part, greater than that of Na_2O.

The P_2O_5 content in the upper horizons is often poorer than in the lower ones. This can be seen very clearly in profile 4. In profile 3, sharp differences in the P_2O_5 content are apparent in horizons I and II. These figures, of course, represent the entire quantity of P_2O_5 found in the horizons and not that which is assimilated by the plants.

Zvorykin (39) conducted investigations in the Moravian Karst on soils formed from red loam overlying hard Devonian limestone. These soils developed zonal characteristics—podzolic and degraded rendzina—under the influence of local physico-geographic conditions. The results of these investigations can be compared with those obtained in Attica by the writers.

The podzolized soils of the Moravian Karst infrequently retain the reddish tinge in horizon A_2, notwithstanding the leaching out of R_2O_3 from the surface layers of the profile. Horizon B resembles "terra rossa" in its color but is distinguished from it by its nutty structure (plate 1, fig. 3). The B horizon of slightly degraded rendzina is still more similar to the red soil formations observed in Attica.

The reddish clay of the Moravian Karst (horizon B) is far richer in Al_2O_3 but much poorer in $CaCO_3$ than are the profiles of Attica that were studied. Similar results, based on total analyses, are found in horizon B of slightly degraded rendzina soils of the Moravian Karst region (table 4).

From a comparative study of the soils of Attica and of the Moravian Karst we observe that the composition of the red soils varies considerably with the physico-geographical condition, notwithstanding the underlying limestone parent material. The data of Reifenberg corroborate this conclusion.

The results of base-exchange determinations on the soils of Attica (table 5) reveal the following phenomena: notwithstanding the large quantities of limestone, as shown by the total analyses, the amount of absorbed Ca is relatively small; absorbed Mg is also found in small quantities; and the Na content is too small to impart to the soil solonetzic properties.

The reaction of the profiles of Attica, expressed in pH, is neutral or slightly alkaline.

From the data in tables 6 and 7 we can compare the exchangeable base content of the soils of Attica with those of the Moravian Karst and Thessalia. The soils of Thessalia, which are reddish brown, rest on soft limestone. In this manner we can compare, on the one hand, the properties of soils found under different climatic conditions, such as the soils of Attica and the Moravian Karst, and, on the other hand, the soils of Attica and Thessalia found under nearly identical climatic conditions, the difference being of a petrographical nature.

From tables 6 and 7 it is apparent that the podzolic horizons of the Moravian Karst profile, as would be expected, are unsaturated with bases and have

a low pH, but the underlying horizon B is of an entirely different character. In this case the quantity of bases rises sharply, and judging from the pH of the soil it is fully saturated with bases. Horizon B, 43–79 cm. a very slightly degraded rendzina soil, is practically saturated with bases, and has a higher index of pH.

In this manner under the same physico-geographic and petrographic condition and environment of the soils, we observe the same degree of saturation with bases, regardless of the different losses of organic matter on ignition.

TABLE 4

SiO_2 and Al_2O_3 extracted with 5 per cent KOH from Moravian Karst soils

MORAVIAN KARST	HORIZONS	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Podzolic soil (degraded rendzina)	A_1	3–8	76.28	12.74	3.83	0.64	0.67	....
	A_2	8–23	78.93	13.12	4.74	0.66	0.88	....
"Terra rossa"	B	23–52	62.73	22.59	5.52	1.67	1.51	0.11
"Terra rossa" of slightly degraded rendzina	B	43–79	63.66	18.29	8.06	2.06	1.39	0.26

TABLE 5

Exchangeable bases of Attica soil profiles

ATTICA	HORIZONS	Ca	Mg	Na	Ca	Mg	Na	TOTAL EXCHANGEABLE BASES	pH
	c.m.	*per cent*	*per cent*	*per cent*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
Profile of Agios Andreas	0–10	0.669	0.017	0.007	33.45	1.41	0.32	35.18	7.38
	10–32	0.578	0.014	0.008	28.90	1.16	0.36	30.42	7.53
	32–60	0.396	0.022	0.005	19.80	1.83	0.22	21.85	7.53
	60–120	0.426	0.017	0.012	21.30	1.41	0.52	23.23	7.60
Profile of Halandri	0–27	0.481	0.024	0.004	24.05	2.00	0.17	26.22	7.57
	27–43	0.449	0.058	0.003	22.40	4.83	0.13	27.36	7.53
	43–55	0.327	0.010	0.003	16.35	0.83	0.13	17.31	7.42
	55–85	0.448	0.048	0.008	22.40	4.00	0.36	26.76	7.20
	85–120	0.213	0.034	0.010	10.65	2.83	0.43	13.91	7.16

The base saturation of the red horizons of the Moravian Karst soils exceeds considerably that of the soils of Attica, notwithstanding the fact that the latter are enormously rich in $CaCO_3$ and contain a considerable quantity of organic matter. The degree of saturation of the soils from Thessalia is also considerably higher than is that of the soils from Attica, which prove to be the poorest of all the soils so far studied by us.

We are of the opinion that the degree of saturation depends not only on the quantity of organic substances, clay, and $CaCO_3$ present, as stated by Mattson

(22) and Williams,[4] but also on the physico-geographic conditions, especially of the "soil climate," as it is termed by Novak (24), and on the degree of solubility of the limestone upon which the soil rests.

One may assume that the degree of solubility is higher for the soft limestones than for compact and hard ones. Sigmond (31) supports this opinion in his study of the application of the methods of Hissink for the exchangeable bases of soils containing large quantities of $CaCO_3$. It is possible, therefore, that the presence in Greece of rendzina found on soft limestone may be explained by the high solubility of the latter. For this reason the rendzina, but not the red soil, has a high content of absorbed calcium.

TABLE 6

Exchangeable cases of Moravian Karst soils

MORAVIAN KARST	HORIZONS	DEPTH	Ca	Mg	Ca	Mg	TOTAL Ca AND Mg	pH	LOSS OF ORGANIC MATTER ON IGNITION
		c.m.	*per cent*	*per cent*	*m.e.*	*m.e.*	*m.e.*		*per cent*
Podzolic soil (degraded rendzina)	A_1	3–8	0.135	0.004	6.75	0.33	7.08	5.00	8.65
	A_2	8–23	0.153	0.007	7.65	0.05	7.70	5.05	4.92
"Terra rossa"	B	23–52	0.843	0.001	42.15	0.08	42.23	6.90	11.04
"Terra rossa" of slightly degraded rendzina	B	43–79	0.813	0.009	40.65	0.73	41.48	7.58	6.95

TABLE 7

Exchangeable bases of Thessalia soil profile

THESSALIA	HORIZONS	DEPTH	Ca	Mg	Na	K	Ca	Mg	Na	K	TOTAL EXCHANGEABLE BASES	pH
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
Profile of Larissa	I	0–12	0.930	0.026	0.024	0.158	46.53	2.18	1.04	4.07	53.82	7.70
	II	12–35	0.949	0.202	0.028	0.183	47.49	16.71	1.21	4.68	70.09	7.64
	III	35–69	0.6257	0.122	0.021	0.180	32.28	11.00	0.91	4.61	48.80	7.74

The presence of organic matter is influenced by the degree of saturation of the soil with calcium, as has been shown in an earlier publication (39).

We believe that the causes of the higher or lower degree of base saturation of soils, even if they are within the limits of the same climatic zone, represent a very complicated question and depend on a series of complex conditions that must be treated separately.

Table 8 presents the determination of SiO_2 and Al_2O_3 extracted with a 5 per cent solution of KOH from soils of Attica. An analysis of these figures shows that SiO_2 and Al_2O_3 are present in very small amounts. In this respect

[4] Unpublished results, cited by Robinson (29).

the red soils under investigation are similar to black earths [see records of Gedroiz (10)].

In combining the figures of SiO_2 and Al_2O_3 into a compound $2SiO_2 \cdot Al_2O_3$ we will always have some SiO_2 unaccounted for, and in some cases, also free Al_2O_3.

The results of table 8 indicate that the soils under investigation were not subjected to the influence of absorbed Na and that the colloidal part of the soil is not easily decomposed even under the influence of the processes of soil formation of Attica.

In studying the red soils of Macedonia, which contain large quantities of Na,[5] we have obtained larger quantities of SiO_2 than of Al_2O_3 even in the case of soils that contained $CaCO_3$.

Zvorykin (39), studying degraded rendzina and podzolic soils in Middle Europe, obtained much higher quantities of Al_2O_3 than in the red soils of Attica; these results are typical for the podzolic zone.

TABLE 8

SiO_2 and Al_2O_3 extracted with 5 per cent KOH from Attica soils

ATTICA	HORIZONS	SiO_2	Al_2O_3	$2S:O_2 \cdot Al_2O_3$	RESIDUE	
					SiO_2	Al_2O_3
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Profile of Agios Andreas	0–11	0.266	0.217	0.471	0.011	.....
	10–32	0.325	0.266	0.578	0.010	.....
	32–60	0.279	0.186	0.401	0.059	.....
	60–120	0.434	0.275	0.534	0.089	.....
Profile of Halandri	0–27	0.348	0.240	0.522	0.065	.....
	27–43	0.437	0.347	0.755	0.020	.....
	43–55	0.523	0.474	0.967	.....	0.029
	55–85	0.473	0.509	0.872	.....	0.108
	85–120	0.465	0.348	0.757	0.055	.....

DISCUSSION

From a comparison of the morphology and the chemical composition of the soil profiles of Attica with those of Thessalia and Middle Europe, the following conclusions can be drawn:

The profiles of the red soils of Attica possess different degrees of maturity related mainly to the topographic conditions of deposition. Profile 3 is less mature than profile 4, as shown by its morphology. In the lower part of the first horizon of profile 3, rough remnants of limestone and secondary formations, in the shape of concretions, are present, which indicates that the process of soil formation is not yet completed.

Profile 4 has fully developed horizons, with small, rather deep concretions. At a depth of 55 cm., we find lime veins; and at 85 cm., a hardpan of limestone impenetrable to the roots is formed.

[5] See footnote 1.

The chemical analyses of both profiles, together with observation *in situ*, indicate an accumulation of lime in the deeper horizons.

The form and distribution of the accumulations of lime in a profile lead us to believe that these are products of the eluvial process that takes place during the wet season of the year. This process apparently is only slightly developed because of the poverty of soil moisture and because of the fact that the secondary products lie very near to the surface.

The comparative records of the Moravian Karst "terra rossa" show that under different physico-geographic conditions, eluviation processes are more marked and therefore no secondary products in the form of concretions occur; the $CaCO_3$ is very energetically washed out. In illuvial horizons of "terra rossa" of the least degraded rendzina soil, however, we encounter large fragments of limestone, covered on the lower surface with a thin, broken, tough crust.

In the more podzolic varieties, the eluvial process is accompanied by an accumulation of Fe_2O_3 and especially of Al_2O_3 in the lower horizons, as is shown by total chemical analyses. By the eluvial process the red clay "terra rossa" of the Moravian Karst is substantially transformed into a podzolic type.

On the other hand, we note the comparatively small accumulation of Al_2O_3 and especially of Fe_2O_3 on the upper horizons of the soils of Attica. This indicates that the illuvial horizon (that enriched with Fe_2O_3 and Al_2O_3) is located near the surface of the soil and corroborates the opinion of Reifenberg (28) concerning the formation of red soils. This small accumulation of Al_2O_3 and Fe_2O_3, regardless of the high evaporation can be explained, in our opinion, by the comparatively small amount of soil moisture and by the duration of the dry hot season, which results in but slight destruction of the soil colloidal particles which are protected by the absorbed calcium.

The red soils of Attica are less saturated with bases than are those of the Moravian Karst; this condition is due, not to the quantity of organic matter present, but to the dryness which retards the reactions that go on in the soil. Sokolovsky (34) shows that in soils formed under dry conditions, we find no considerable quantities of adsorbed calcium, notwithstanding the presence of large quantities of $CaCO_3$.

The augmented quantity of adsorbed bases has been pointed out by Gorshenin (13), who studied the phenomenon of degradation of the Siberian black soils and has explained this phenomenon on the basis of the influence of moisture and humification of black soils under forest conditions. Our investigation with soils of Attica under similar conditions corroborates the results obtained by Gorshenin.

The first horizon of profile 3 is more saturated with bases than is that of profile 4. Since we have studied a rather limited number of samples, we cannot state definitely the influence of the forest soils upon the degree of saturation with bases for the soils of Attica.

On the basis of soil extraction with 5 per cent KOH of profile 4, we concluded that the hardpan of the soil owes its origin, not to the saturation with sodium but to the accumulation of lime, such formations being typical for the soils of dry regions.

We are of the opinion that it is rather unreasonable, because of the slight saturation with bases, to compare, as Stebutt (35) does, the brown earths of Ramann with the red soils of the dry regions of the Mediterranean. In our studies of the brown earths of Middle Europe we found either podzolic soil varieties of forest soils or degraded black earths. In such cases an accumulation of R_2O_3 is encountered in the lower horizons but never in the upper ones as in the red soils of Attica. This is proved by the analytical records of Stremme (38) and of Smolik (32).

The comparatively feeble saturation with bases of the brown earth is accounted for by the podzolic process which often reaches a very advanced state. In Attica the degree of saturation is very likely combined with more complicated circumstances, as has been partially described. Apart from this we must take into consideration the remark of Glinka (12, p. 414) that under the name of "brown earths" are seemingly described various soil formations; as an example, we can take the map of Stremme (37, p. 18).

In such a manner, if we agree to call "brown earth" every feeble podzolic soil tinted with brown and brownish hues then of course the red soils of Attica have very little in common, as to origin, with the podzolic soils.

The phenomenon of podzolization of the red-tinted soils of Middle Europe indicates their ancient origin.

From our studies of the Greek red soils in the vicinity of Salonica we can indicate their age by their salinity. This process of salinity goes on in the red soils situated on terraces surmounting the valley of the Vardar River. This valley was occupied during the diluvial period by a very large salt lake (3). During this period the ground-water level was higher in the region of these terraces; only under similar conditions could the rise of salts have taken place. As a result of this process spots of solonetz and degraded solonetz soils are found up to this day.

The saturation of this type of red soils with sodium originates with the predominance of the eluvial processes. We may therefore observe a compact impervious illuvial horizon, enriched with organic matter and R_2O_3 which are normally found on the lighter leached eluvial horizon. This phenomenon is reversed for the red soils of Attica that are not saturated with sodium.

The "solodi" varieties of red soils possess an acid reaction and in their morphology resemble the feeble podzolic brown earth of Ramann but have an entirely different origin. On this account it is not surprising to note that such soils had been mapped as brown earths.

We think that the study of the cycles of erosion in the Mediterranean region, and in Attica in particular, can disclose with a higher degree of accuracy the age of the red soils than of those that underlie the parent rock.

As has already been stated, the investigation of the origin and properties of

red soils is a very complicated task, in as much as it requires the study of factors that present considerable difficulties.

It seems to us that considerable difference of opinion as to the origin of the red soils is due to the absence of systematic studies of the Mediterranean region. This difference of opinion is accounted for by climatic conditions, topography, erosion, saturation processes with sodium, solodi and podzolic processes. The last condition can take place in regions of abundant rainfall (in some Mediterranean regions this reaches 800 mm.) and in regions situated high above sea level. The variety of conditions noted seemingly causes variation in the character of the red soils, not only in different latitudes and altitudes, but even within the boundaries of a small region whose soil-forming history is very old.

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PLATE 1

FIG. 1. Profile of Agios Andreas
FIG. 2. Profile of Halandri
FIG. 3. Profile of Moravian Karst (Podzolic Soil)

FIG. 1

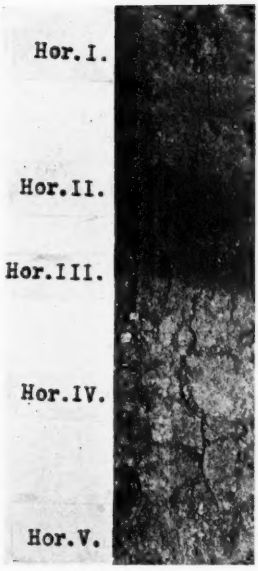

FIG. 2

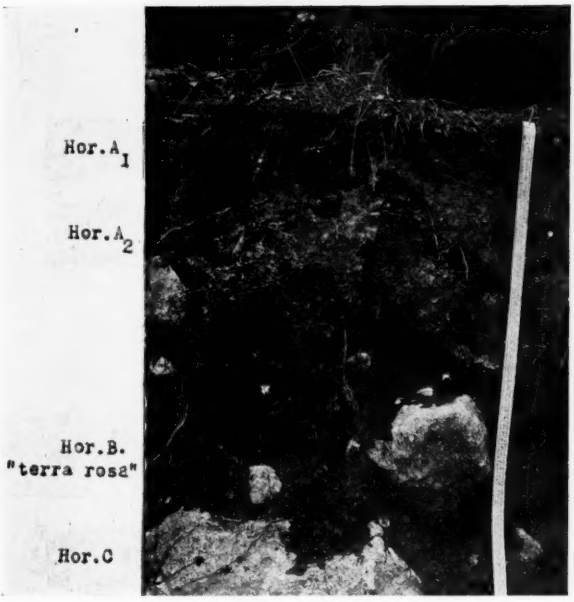

FIG. 3

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PLATE 2

FIG. 1. Concretions in the Profile of Agios Andreas
FIG. 2. Remnants of Limestone in the Profile of Agios Andreas

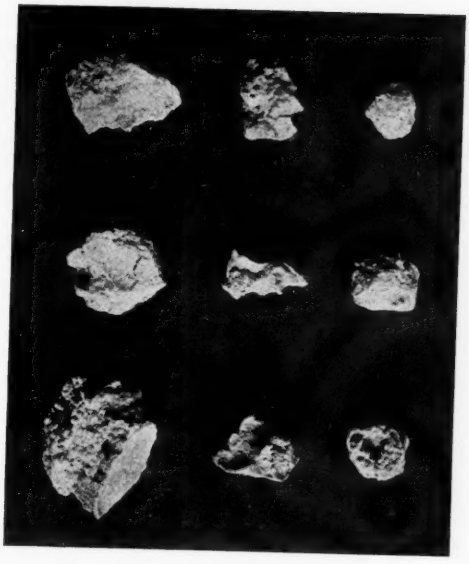

FIG. 2

FIG. 1

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THE COMPOSITION AND IONIC EXCHANGE OF FERRIC SILICATES AND PHOSPHATES[1]

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Since Way (18) demonstrated the base exchange capacity of soils, many workers, especially Wiegner (19), Hissink (7), Gedroiz (4), Kelley and Brown (9), and Mattson (10), have contributed to the general knowledge of the subject. It is evident, however, that there is a lack of unanimity as to the true mechanism of the reaction, partly because the composition of the colloidal anion is unknown.

It has been generally supposed that the acidoid component of the soil colloid is composed chiefly of silica and phosphoric acid, the part played by the hydroxyl group being usually neglected. Both the phosphate and the silica are combined with ferric iron or alumina, which forms the basoid part of the giant molecule, although other elements are present in smaller amounts. The composition of the soil colloid is extremely complicated, but a study of silicates and phosphates in their simplest form would materially aid in elucidating analogous phenomena such as occur in the soil.

EXPERIMENTAL

Preparation of ferric silicates. A normal solution of ferric chloride was titrated against a solution of sodium silicate of known silica content until the iron was completely precipitated, which occurred at pH 5.4–5.6. To obtain precipitates of lower $\frac{SiO_2}{Fe_2O_3}$ ratio, the amount of sodium silicate was progressively reduced, the amount of reduction being made up with *N* NaOH until a pH of 5.4 was again reached. To obtain precipitates of high $\frac{SiO_2}{Fe_2O_3}$ ratio, the amount of sodium silicate was kept constant, but the ferric chloride was reduced, the diminished acidity being made up with *N* HCl to bring the whole, when mixed, to pH 5.4. By means of preliminary titrations the exact amounts of reagents required to fulfill the aforementioned conditions were determined.

The solutions were mixed by rapid pouring from one beaker to the other, and the floc was allowed to settle for one hour and was then filtered. To

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

prevent extensive hydrolysis, the precipitates were washed free of chlorine with 95 per cent alcohol; the residual alcohol was removed by drawing a current of air through the filter.

Base exchange. Two samples of the precipitate prepared as described were weighed. The dry matter was determined on one of them at 105°C. The base exchange capacity was determined on the other by leaching with *N* Ba-acetate (pH 7.0) until the pH of the leachate was equal to the pH of the original Ba-acetate. Ten cubic centimeters of *N* $BaCl_2$ was then added to the filter, and the precipitate was washed free of chlorine with water. The adsorbed barium was subsequently replaced with *N* NH_4Cl, and the base exchange capacity was calculated to a constant weight of the dry material.

Exchange neutrality.[2] A 1 per cent suspension of the colloid was prepared, and 50 cc. of the suspension was added to 100 cc. of a mixed solution of sodium sulfate, sulfuric acid, and sodium hydroxide contained in a 200-cc. flask. The sulfate concentration was kept constant, and the total volume of colloid and salt solution was made up to 200 cc. The quantity of sulfate adsorbed was taken as the difference between the sulfate content of the original solution and that of the supernatant liquid. The pH after attainment of equilibrium was determined on the suspension with the quinhydrone electrode, and the pH of the salt solutions was determined at identical dilutions colorimetrically.

Ferric phosphates. The procedure adopted for the precipitation of ferric phosphates was identical with that used for the silicates. A solution of normal sodium hydrogen phosphate completely precipitated the iron from a ferric chloride solution at pH 4.3. By substituting sodium hydroxide for sodium phosphate the quantity of phosphate in the precipitate was varied as in the case of silicates.

DISSOCIATION OF AMPHOTERIC ELECTROLYTES

All amphoteric electrolytes are defined as compounds that possess both acid and basic properties and that on dissociation provide both hydrions and hydroxyl ions. An alternative suggestion has, however, been made, that is, that an amphoteric electrolyte is a compound that can both combine and provide hydrions. For a discussion on the definition of acids and bases the reader is referred to Davies (2), but the following discussion of amphoteric electrolytes is paraphrased from the work of Michaelis (12, p. 61–66):

If the ampholyte is present in solution in concentration [A], as an acid it forms anions of $[A^-]$ concentration, and its acid dissociation constant is k_a. It can also function as a base of dissociation constant k_b, and forms cations of $[A^+]$ concentration. The ratio of the undissociated portion to the total concentration [A] of the ampholyte is given by the expression:

$$\rho = \frac{[A] - [A^+] - [A^-]}{[A]}$$

[2] This term is used by the authors in a sense not strictly comparable to that used by Mattson, who originated this term. In our case the displaceable cations or anions have not been removed by electrodialysis.

The degree of dissociation must be given separately for the cations and anions and is

$$\alpha^- = \frac{[A^-]}{[A]} \text{ for the anions, and } \alpha^+ = \frac{[A^+]}{[A]} \text{ for the cations.}$$

From the law of mass action

$$[A^-] \times [H^+] = k_a \times [U] \qquad (A)$$

where U is the undissociated portion of the ampholyte, and furthermore,

$$[A^+] \times [OH^-] = k_b \times [U] \qquad (B)$$

It follows, therefore,

$$A^- = \frac{k_a [U]}{[H^+]}$$

$$A^+ = \frac{k_b [U]}{[OH^-]}$$

and

$$[A] - [A^+] - [A^-] = U = [A] - k_a \frac{[U]}{[H^+]} - k_b \frac{[U]}{[OH^-]}$$

From which it follows

$$U = \frac{[A]}{1 + \frac{k_a}{[H^+]} + \frac{k_b}{[OH^-]}}$$

and hence the sought value of ρ may be stated as

$$\frac{[U]}{[A]} = \rho = \frac{1}{1 + \frac{k_a}{[H^+]} + \frac{k_b}{[OH^-]}}$$

Substituting for $[OH^-]$ its value as $\frac{k_w}{[H^+]}$ we obtain:

$$\rho = \frac{1}{1 + \frac{k_a}{[H^+]} + \frac{k_b}{k_w}[H^+]}$$

The maximum of the ρ^- curve can most easily be calculated as the minimum of the inverse function

$$\frac{1}{\rho} = 1 + \frac{k_a}{[H^+]} + \frac{k_b}{k_w} \cdot [H^+]$$

and

$$\frac{d\frac{1}{\rho}}{d[H^+]} = -\frac{k_a}{[H^+]^2} + \frac{k_b}{k_w}$$

and

$$[H^+] \text{ for } \rho - \text{max.} = \sqrt{\frac{k_a}{k_b} \cdot k_w}$$

The isoelectric point I is, therefore, at that $[H^+]$ which is determined by the equation

$$I = \sqrt{\frac{k_a}{k_b} \cdot k_w}$$

The most important characteristics of the isoelectric point are: 1. At the isoelectric point the sum of the anions and cations of an ampholyte in a given concentration is at a minimum. 2. The concentration of the anions of an ampholyte at its isoelectric point is equal to that of the cations.

These conditions can be proved from equations *A* and *B*.

$$[A^-] = \frac{k_a \cdot [U]}{[H^+]} \text{ and } [A^+] = \frac{k_b \cdot [U]}{[OH^-]}$$

By substituting for $[H^+]$ its value at the isoelectric point, and for $[OH^-]$ the corresponding value

$$\frac{k_w}{[H^+]} = \frac{k_w}{\sqrt{\frac{k_a}{k_b} \cdot k_w}} = \sqrt{\frac{k_b}{k_a} \cdot k_w}$$

we obtain

$$[A^-] = [U] \cdot \frac{k_a}{\sqrt{\frac{k_a}{k_b} \cdot k_w}} \text{ and } [A^+] = [U] \cdot \frac{k_b}{\sqrt{\frac{k_b}{k_a} \cdot k_w}}$$

Therefore $[A^-] = [A^+]$

There are, however, two large groups of ampholytes: those in which the acidic and basic radicals are spatially apart, such as the amino acids and proteins, and those in which the two radicals are one and identical, such as the metal hydroxides. Michaelis assumes the formation of an inner salt to explain the amphoteric behavior of the former, whereas the dissociation of a hydroxyl ion on the one hand and a hydrion on the other is sufficient to explain the amphoteric behavior of the latter. The strength of the ampholyte as an acid or base is determined by the ratio of $\frac{k_a}{k_b}$, but all acids or bases are probably amphoteric to a greater or lesser degree.

REPLACEMENT OF SiO_3 AND PO_4 BY THE OH ION

The composition of the silicates varies with the proportion of the salts taken. With the ferric phosphates it was found impossible to prepare a compound of $\frac{PO_4}{Fe_2O_3}$ ratio higher than 0.71, for the compounds decomposed until this ratio was formed.

In a previous discussion on phosphates by Mattson (10) and the senior author (14), emphasis was laid on the fact that for the precipitation of phosphatic compounds a certain concentration of hydroxyl ions is required to prevent acid hydrolysis. The requisite concentration depends on the nature of the compound, being higher for aluminum phosphate than for ferric phosphate.

At a certain pH range the precipitation of phosphate was increased by increasing the pH, but when the pH was further increased, the phosphate content of the precipitate was reduced, the $PO_4^{=}$ being replaced by OH^-. The pH of precipitation in these experiments was originally chosen in order to give a compound of maximum insolubility, as denoted by the complete precipitation of iron. All the compounds were precipitated at this pH, but varied in composition, as sodium hydroxide was used instead of sodium silicate.

This relationship between the concentration of the silicate solution and the molecular ratio of the precipitate is perfectly linear, and so also is the rela-

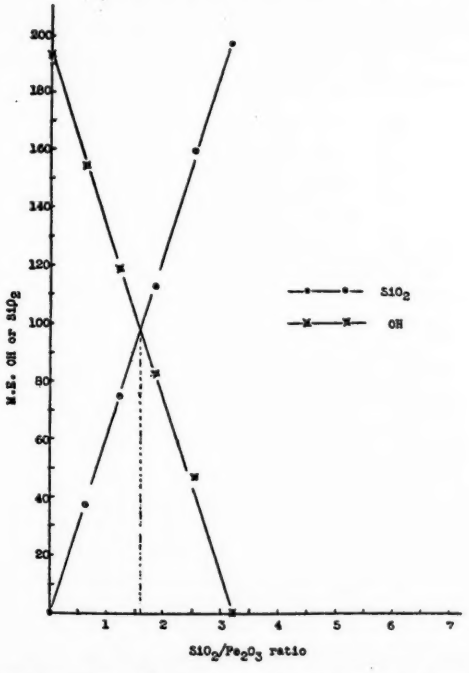


FIG. 1. RELATION BETWEEN OH, SiO_2, AND COMPOSITION OF FERRIC SILICATES

tionship between the concentration of hydroxyl ions and the composition of the precipitates (fig. 1). There is another fact that is apparent, that is, the slopes of the lines are identical in both cases, but the graph connecting the concentration of hydroxyl ions with the composition of the precipitate is an exact mirror image of the graph connecting the concentration of the silicate ions with the composition of the same precipitate. This interrelationship is also apparent with the phosphatic compounds, where the graphs connecting the concentration of $[OH^-]$ and $[PO_4^{=}]$ ions with the molecular ratio of $\frac{PO_4}{Fe_2O_3}$

of the precipitates are exact mirror images (fig. 2). Consequently, the hydroxyl ion is replacing the [SiO_3^-] and [$PO_4^{\equiv}$] ions in exactly equivalent proportions. Silicates and phosphates can therefore be regarded as substituted hydroxides, a fact which is of great importance for the interpretation of base exchange.

THE SiO_2 RATIO / Fe_2O_3

The composition of the clay complex of the soil varies with its stability under climatic conditions and the reaction of the medium. According to Mattson (10) the composition of the colloid and its pH so strongly influence each other that it is difficult to distinguish between the cause and the effect. Of particular interest from the viewpoint of the chemistry of silicates are the laterites

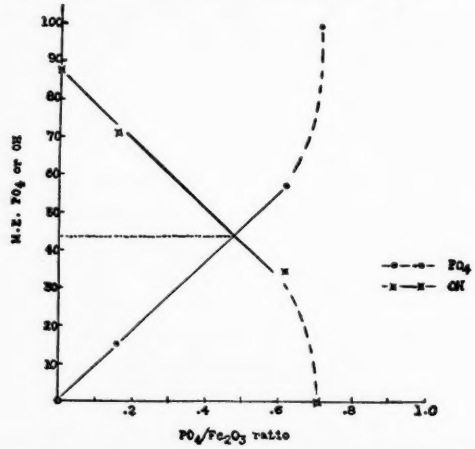


FIG. 2. RELATION BETWEEN OH, PO_4, AND COMPOSITION OF FERRIC PHOSPHATES

and podzols, the chemistry of development of which has been discussed by numerous workers such as G. W. Robinson (16), Jones and Wilcox (8), and Reifenberg (15).

The development of both podzols and laterites can well be interpreted from the behavior of the ferric silicates. Although it is true that alumina is the chief basoid component of soils, there is always a high percentage of iron, and the behavior of aluminum and ferric silicates is so similar that what applies to one can also apply to the other. The ferric silicates, whatever the concentration of silica, could not completely precipitate the iron until pH 5.4 was reached. This is the synthetic counterpart of acid hydrolysis or podzolization. By maintaining the concentration of ferric chloride constant and precipitating the iron at pH 5.4 with a mixture of silica and hydroxyl ions, so that the product [OH^-][SiO_3^-] in equivalent concentration is always constant, a series of com-

pounds is obtained with varying quantities of silica as shown in figure 1. This is the synthetic equivalent of laterization where the silica can be replaced in part or completely by hydroxyl ions until ferric hydroxide is formed.

Mattson (10), in a theory of isoelectric weathering, put forward the suggestion that amphoteric soil colloids alter their composition in such a way that their isoelectric points coincide with the prevailing pH. In laterites under conditions of high rainfall the bases are dissolved; consequently, the prevailing pH initially will be alkaline and will become acid as the leaching of the bases continues. Since bases are again returned to the soil in considerable quantities by the plants, there are alternations of alkalinity and acidity in these soils. Under alkaline conditions ferric silicates are not stable, the hydroxyl ion replacing the SiO_3. The two compounds which originate by hydrolysis and are stable under such conditions are ferric and aluminum hydroxide, the isoelectric points of which when prepared from their chlorides are at pH 7.1 and pH 8.2 respectively. This theory gives a reasonable explanation for the exist-

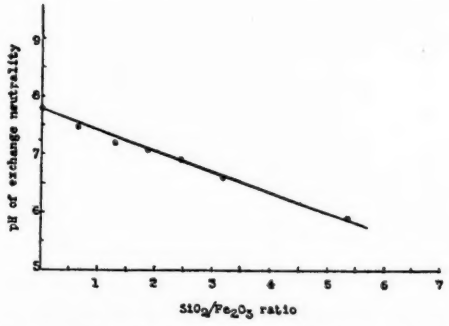


FIG. 3. RELATION BETWEEN SiO_2/Fe_2O_3 RATIO AND pH OF EXCHANGE NEUTRALITY

ence of the hydrous oxides of both iron and aluminum in the free state in these soils.

The relationship between the composition of the precipitates and their pH of exchange neutrality is shown in figure 3. With increasing silica content of the precipitate the lower becomes the pH of exchange neutrality, which represents the most stable pH zone for that compound. At pH 7.8 the most stable compound formed with ferric iron in the presence of SiO_2 and OH ions is ferric hydroxide.

There are cases, however, in soils of the lateritic type where there is considerable evidence of the mobility of the sesquioxides, which is attributed by Campbell (3) to the alkalinity of the ground water and by Harrassowitz (5) to the protective effect of silicic acid sols. The fact that in some lateritic soils there is considerable accumulation of free sesquioxides does not mean that they are stable under all conditions under which typical laterites are formed. The zone of precipitation of these hydroxides with respect to pH is extremely

narrow, and they are readily soluble in an excess of acidity or alkalinity as compared with their isoelectric pH. Secondary to desilication, this effect may also proceed, leading to a rather complete destruction of the surface layer in lateritic soils.

EXCHANGE NEUTRALITY AND ADSORPTION OF SULFATE WITH FERRIC SILICATES AND PHOSPHATES

The fact that soil colloids, phosphates, and silicates are amphoteric in behavior leads to both exchange acidity and exchange alkalinity. Both are manifestations of the dissociation of a colloidal electrolyte; in the former case the dissociated hydrion is replaced by the cation of the salt, and in the latter

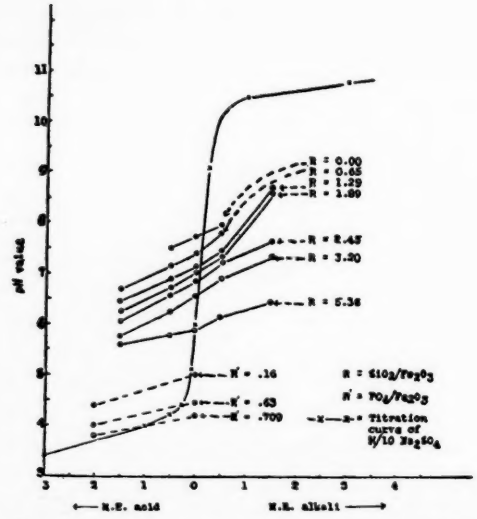


FIG. 4. EXCHANGE NEUTRALITY OF FERRIC SILICATES AND PHOSPHATES

the dissociated hydroxyl ion is replaced by the anion of the salt. This has been found for a large number of compounds by Mattson and Hester (10) and for hydroxides by the senior author (14). The graphs for the exchange reactions with these compounds, using a sodium sulfate solution of varying pH but of constant normality with respect to the sulfate anion, are shown in figure 4.

As has previously been found by Mattson (10), the point of exchange neutrality is consistently displaced to the acid side as the silicate or phosphate content of the precipitate is increased, the replacement of the hydroxyl by the phosphate ion increasing the acid dissociation, a new compound being formed by substitution with a stronger acidic but a weaker basic dissociation.

A remarkable regularity is observed in the adsorption of sulfate by both the

silicates and the phosphates (figs. 5 and 6). Ferric hydroxide has a considerable capacity for sulfate adsorption, but with silicates and phosphates the anion adsorption is greatly diminished, and with silicates of $\frac{SiO_2}{Fe_2O_3}$ ratio 1.89 it is non-existent, although they exhibit marked exchange neutrality. Each

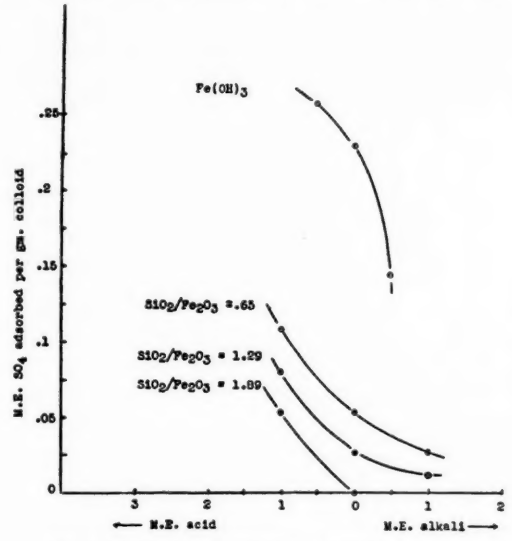


FIG. 5. SULFATE ADSORPTION BY FERRIC SILICATES

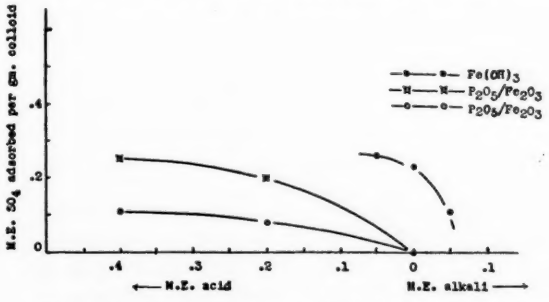


FIG. 6. SULFATE ADSORPTION BY FERRIC PHOSPHATES

component in the colloid influences the dissociation of the other, and increasing the phosphate or silicate content of the colloid by replacing the hydroxyl group appears to be accompanied by a diminished capacity for anion adsorption. As a function of the pH and the isoelectric point, both hydrions and hydroxyl ions are dissociated from the surface of the colloid, but other ions need not of necessity be adsorbed.

BASE EXCHANGE CAPACITY OF FERRIC SILICATES

The base exchange capacity of the ferric silicates determined as previously described is represented graphically in figure 7. The base exchange capacity increases, as found by Mattson (10) with increasing ratio $\frac{\text{acidoid}}{\text{basoid}}$, reaches a maximum, and then diminishes.

It has been customary in base exchange studies to regard the colloidal fraction of the soil, whether organic or inorganic, as the seat of base exchange reactions, and to consider that the colloids themselves function as weak acids.

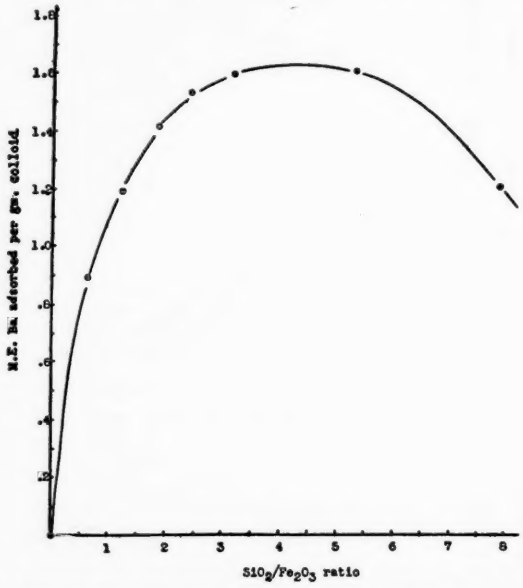


FIG. 7. BASE EXCHANGE IN RELATION TO SiO_2/Fe_2O_3 RATIO AT pH 7

Bradfield (1) has suggested that the best method for determining the intensity or the strength of the acids is by the use of some expression analogous to the dissociation of weak acids, which is obtained from the mass action law and is given the expression

$$pK = pH + \log \frac{\text{salt}}{\text{acid}}$$

At the point of half neutralization the last term becomes 0 and the apparent pK value is numerically equal to the pH value at that point.

Wiegner (19) represents the particle of the inorganic soil colloid as if it were a crystal, but the double layer surrounding the micelle is composed of

two swarms forming an inner and outer layer of hydroxyl and hydrogen ions. If the outer layer is composed of hydroxyl ions, then exchange alkalinity is supposed to take place with a salt solution, but if the hydrions form the outer layer, then exchange acidity takes place, the hydrion being replaced by the cation of the salt.

The strength of ordinary acids at equivalent concentration can be determined with considerable accuracy from conductivity determinations, but this is only possible because the hydrogen ion has a much higher mobility than any anion. For amphoteric electrolytes, which, depending on conditions, dissociate the highly mobile hydroxyl ion as well, such a method cannot be applied, but the method of Michaelis of determining the isoelectric point with respect to the pH does give the requisite information and also a means of determining the relative strength of amphoteric compounds both as acids and bases.

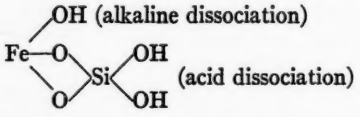
Regarding both silicates and phosphates as substituted hydroxides, as shown in figures 1 and 2, permits of a somewhat easier interpretation of both the origin of charge and the nature of base exchange reactions than was hitherto possible. It has previously (14) been stated that although hydroxides at their isoelectric pH have no base exchange, substituted hydroxides in soil, such as phosphates and silicates, if leached with a salt solution of the same pH, have base exchange under the same conditions, although below the isoelectric pH it becomes an absolute minimum. If these compounds are regarded as substituted hydroxides of the form $X(OH)$ (SiO_2H_2), such a phenomenon can be readily understood. If ferric hydroxide is treated with a solution of pH 7.2, there is in the solution a sufficient pressure of hydrions and hydroxyl ions to prevent the dissociation of either from the colloid. Even in substituted hydroxides the bond between the Fe and OH will be the same as in the pure hydroxide, but since some of the hydroxyl groups have been replaced by the acid PO_4 and SiO_3 groups, which dissociate hydrions from the surface, the substituted colloid will have a new isoelectric pH when the acid dissociation of the acid groups will be counterbalanced by the basic dissociation of the residual undisplaced hydroxyl groups. As more acid groups are introduced, the isoelectric pH of the colloid will be at a lower pH than that of a higher hydroxyl content, so as to permit an increased dissociation of hydroxyl groups to counterbalance the greater acid dissociation introduced by the substitution. Since both the dissociation of the hydroxyl and the acid dissociation of the other groups are a function of the pH, lowering the pH increases the former but suppresses the latter. With hydroxides both the acidic and basic dissociations arise from the dissociation of a single group [X-O-H]. With silicates, phosphates, and proteins the acidic and basic groups are spatially apart, but both are united directly with the central atom. An isoelectric point with no dissociation cannot therefore arise with a substituted hydroxide, for the hydroxyl group attached to the central atom is un-ionized only at the isoelectric pH of the hydroxide, but is ionized at a lower pH. The isoelectric point of a substituted hydroxide is at a pH where the concentration of hydrions and

hydroxyl ions is such that the dissociation of hydrions from the acid group balances the dissociation of the non-substituted hydroxyl ions.

With the ferric silicates under consideration, an extremely high ratio of $\frac{SiO_2}{Fe_2O_3}$ is required before the complete replacement of the hydroxyl groups is obtained, but with soils in which the ratio is much lower, the substitution is incomplete, and therefore most soils have an exchange alkalinity as well as an exchange acidity. The nearer the substitution of the hydroxyl groups by acid groups is to completion, the more likely the soil is to function completely as an acidoid without any perceptible basic dissociation, which is the case with soil colloids of extremely high silica content, such as bentonite. The higher the silica content of any silicate the higher therefore will be its saturation capacity at pH 7.0, provided that the stability of the compound is unchanged as the dissociated hydrions are replaced by the other cations.

In this respect silicic acid occupies a remarkable position. Electrokinetically, silicic acid always functions as an acidoid, but it is extremely unstable and breaks up into H_2O and SiO_2 units. The SiO_2 is an ion $:\ddot{O}:Si:\ddot{O}:$ in which the oxygen has an excess of valency electrons or more than is required to balance the charge on its nucleus, and it has therefore a potential capacity for cation adsorption. Such a compound, however, is unstable, as, probably because of the unsaturation of the silicon atoms, the lone pairs of electrons of the oxygen are utilized in the polymerization of the SiO_2 as described previously and are not available for the electrostatic attraction requisite for cation exchange.

With both iron and aluminum the lone pairs of the oxygen atoms of the silicic acid are utilized in saturating the iron and alumina, forming a compound of the following hypothetical structure:



By polymerization a micelle or crystal lattice is formed in which the lone electron pairs of the oxygen atoms of the silicic acid residue are utilized in saturating the iron and aluminum, leading to indefinite polymerization. The iron and aluminum are included, as previously described, in the micelle (14) but with hydroxyl groups at the surface. Since they are substituted hydroxides, a lower concentration of hydroxyl ions is required to form the micelle, and they are always formed and are stable at a lower pH than the hydroxides of the same metal.

With the silicates of high $\frac{SiO_2}{Fe_2O_3}$ ratio, although their points of exchange neutrality are at a low pH, they have under leaching conditions a tendency to

decompose at pH 7.0, some of the silica coming out of combination polymerizing on the surface of the ferric silicate, as does the free silicic acid, and preventing base exchange from proceeding. With the basic silicates, those of low $\frac{SiO_2}{Fe_2O_3}$ ratio, this does not occur, as sufficient ferric iron is present to utilize all the available linkages of the oxygen atoms of the SiO_2, until with increasing ratio more silicon is introduced so as to exceed the maximum co-valency of the iron. The point of maximum base exchange will therefore correspond to that point at which the silica can be used in saturating the iron, and further silicic acid introduced beyond that point gives an unstable combination. An attempt is being made to get a more stable acid than silicic or phosphoric in order to obtain a complete verification of this point.

Representing silicates as has been done above brings them into a class similar to the proteins as far as colloidal properties are concerned. Proteins are formed by the combination of amino acids, and silicates by the polymerization of simpler units, to form a molecule of colloidal dimensions. An amino acid is formed by the substitution of an NH_2 group for a hydrogen atom, and in a similar manner a silicate or a phosphate is formed by the substitution of silicic or phosphoric acid group for a hydroxyl group in a hydroxide in equivalent proportions. By continuous polymerization of the simpler units a micelle of colloidal dimensions is formed which can be broken up into simpler units by hydrolysis, but the iron and alumina can be in either the cationic or anionic parts of the hydrolyzed micelle until complete decomposition takes place.

Although Wiegner (19) represents the particle of a soil colloid with a double swarm of hydrions and hydroxyl ions, the authors find that such a conception does not permit of an adequate theoretical explanation to fit the observed facts, such as the influence and the significance of the pH of the leaching liquid and the isoelectric pH of the colloid itself on the saturation capacity. Michaelis' theory of dissociation as a function of the pH, however, does give the requisite interpretation. The fact that Michaelis derived his theory for soluble ampholytes makes no difference in its application to colloidal electrolytes which have hydroxyl groups at the surface. In both cases the dissociation can be regarded as a surface dissociation which is a function of the pH, and that one forms an insoluble micelle and the other is molecularly dispersed makes no difference as long as the dissociation is regarded as a surface dissociation which is a function of the pH.

The ionic exchange in silicates, phosphates, and hydroxides can be tentatively interpreted on the following bases:

Hydroxides, phosphates, and silicates attain the collodial state by a continuous process of molecular polymerization with the formation of co-valent compounds.

Hydroxides have no base exchange if leached with a solution the pH of which corresponds to the isoelectric pH. When base exchange is taken as a test for ionization of the hydrion, there can be no dissociation at the isoelectric point with hydroxides.

Substituted hydroxides have base exchange if leached with a solution the pH of which cor-

responds to their isoelectric pH, because the isoelectric point is reached when the dissociation of the residual undisplaced hydroxyl groups balances the acid dissociation of the silicic or phosphoric acid residue. The greater the proportion of silicic or phosphoric acid in the compound, the stronger the acid dissociation of the compound and the lower the isoelectric pH. Although there is dissociation at the isoelectric point with substituted hydroxides, it is at a minimum.

The dissociation of either hydroxyl or hydrions from the surface of the micelle is a function of the pH of the solution, and ionic exchange is a secondary reaction.

SUMMARY

Ionic exchange reactions have been studied with synthetic ferric silicates and phosphates. It has been shown that the adsorption of sulfate diminishes with increasing acidoid content of the colloid.

The ferric silicates have an optimum ratio at which the base exchange is a maximum.

The hydroxyl ion displaces the [$SiO_3^{=}$] and [$PO_4^{\equiv}$] ions in equivalent proportions.

The application of the isoelectric point and the theory of amphoteric electrolytes to the interpretation of ionic exchange has been discussed.

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A NEW APPARATUS FOR CARBONIC ACID ESTIMATIONS IN SOILS

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Researches have shown that $CaCO_3$ in the soil performs a variety of functions of the greatest agronomic importance. For example, a serious displacement of calcium from soil colloids by H ions produces acidity, leading to conditions unfavorable for microörganisms as well as for cultivated plants. In arid regions the exchangeable calcium of the soil is often displaced by sodium to a considerable extent, resulting in the production of alkali soils. Moreover, a progressive removal of calcium from the exchange complex may result ultimately in lowering the base-exchange capacity of the soil. The degree of calcium saturation of the soil, together with the amount of a $CaCO_3$ present, is also important in connection with the application of fertilizers and manures.

Gasometric estimations of carbonates in soils are generally made with the apparatus designed by Collins. Although convenient for many purposes, Collins' calcimeter suffers from certain inherent defects. The intervention of a rubber tubing between the reaction flask and the measuring burette may occasionally cause considerable errors. Moreover, since one end of the tube adjacent to the measuring burette is open to the air, the instrument is very sensitive to atmospheric pressure fluctuations. Further, the construction of the apparatus is complex, and a few rubber connections are inevitable. To circumvent these difficulties, a manometric apparatus for carbonic acid determinations was developed in this laboratory and has been in use for some time with satisfactory results. Some of the main advantages of this apparatus are as follows:

It is simple in construction and is easily manipulated.

With a view to precision in measurements, the use of rubber connections in the construction of the apparatus has been avoided.

It is independent of atmospheric pressure variations.

The use of a modified Thunberg tube (4) as the reaction vessel makes it possible to mix the reactants very effectively. Moreover, the detachable nature of this bulb, which can be shaken by hand apart from the apparatus, obviates the necessity of a shaking equipment.

THEORY

The principle of the apparatus is the same as that employed by the authors for another purpose (3). The amount of CO_2 evolved will be proportional to the increase of pressure in the reaction bulb. If h is the increase of pressure

in millimeters of Brodie solution[1] and x is the amount of CO_2 evolved in μl. at N.T.P. (dry), we have

$$x = h.k$$

The value of the constant is calculated from the following simplified (2) formula:

$$k = \left(\frac{Vg \frac{273}{t + 273} + Vf. \alpha_{CO_2}}{P_o} + A \frac{273}{t + 273} \right),$$

where Vg = μl. gas in the bulb down to the zero mark on the manometric tube;
Vf = μl. acid in side tube;
α_{CO_2} = Bunsen absorption coefficient of CO_2 at $t°$;
Po = pressure of one atmosphere expressed in mm. of Brodie solution[2]
A = area[3] of cross-section of manometer tube in sq. mm.

No thermostat is used with the apparatus, but a table is constructed giving the value of the constant at various temperatures from 15° to 35°C. By means of a sensitive thermometer placed in the water jacket, the temperature at which the experiment is being conducted is noted and the value of the constant given against it is utilized in the computation of volumes of CO_2 evolved. After the amount of CO_2 evolved in μl. at N.T.P. has been obtained, the percentage of CO_2 in the soil is easily computed. One μl. of CO_2 at N.T.P. weighs 0.001977 mgm.,[4] and the percentage by weight of CO_2 in the original sample, say x, is given by the following formula:

$$x = \frac{V \times 0.1977}{w},$$

where V = volume of CO_2 in μl. at N.T.P.
and w = weight of the soil sample in mgm.

DESCRIPTION OF THE APPARATUS

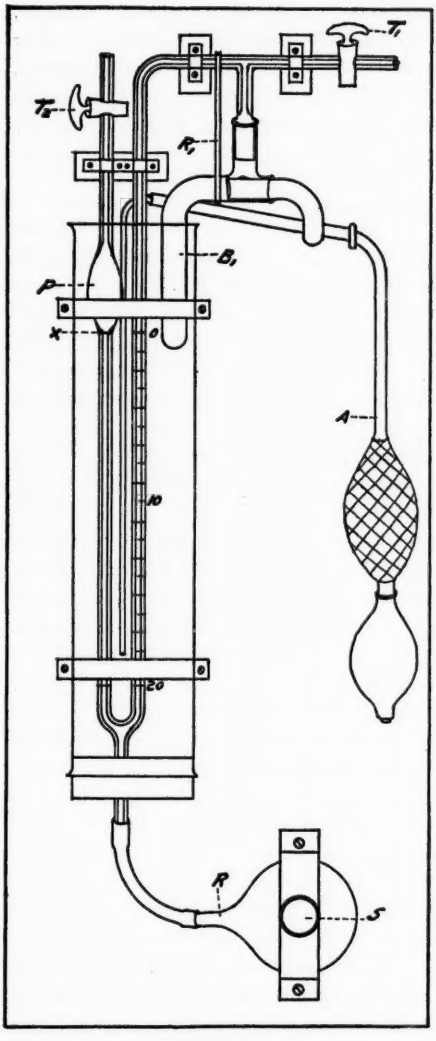
The apparatus (fig. 1) consists of a manometer (with a cross-sectional area not exceeding $\frac{3}{4}$ sq. mm.), on one limb of which a 200-mm. scale is etched. The other limb of this manometer is blown into a bulb (P) and carries a tap (T_2) at its extremity. The circular mark (X) below the bulb (P) corresponds with the zero mark on the manometric scale. A screw-clamp arrangement with a

[1] The composition of Brodie solution is as follows: 500 ml. water, 23 gm. NaCl, 5 gm. sodium tauroglycocholate, and a few drops of an alcoholic solution of thymol.

[2] One atmosphere is approximately equivalent to 10,000 mm. Brodie solution.

[3] It should be clearly recognized that A must be less than $\frac{3}{4}$ sq. mm. In case it greatly exceeds 1 sq. mm., errors of several per cent may be introduced under certain conditions by using the simplified formula given above.

[4] Since the density of CO_2 is 1.529 referred to air as unity and 1 ml. of air at N.T.P. weighs 0.001293 gm., evidently 1 ml. CO_2 will weigh 0.001977 gm. at N.T.P.



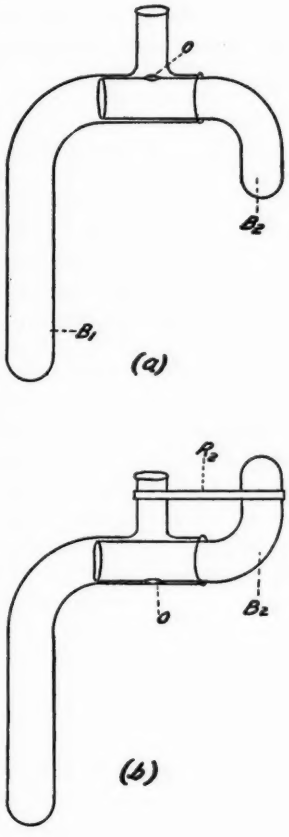


FIG. 1 FIG. 2

FIG. 1 APPARATUS FOR CARBONIC ACID ESTIMATION IN SOILS
FIG. 2 MODIFIED THUNBERG TUBE

rubber reservoir (R) is also provided, the manometric liquid being adjusted by means of a screw (S). The reaction bulb (fig. 2a) used is a modification of the Thunberg tube (4) and has a capacity of 30–35 ml. Through the tap (T_1) the

pressure inside the manometer is equilibrated with the atmospheric pressure. The various parts of the apparatus are enclosed within a glass jacket, the water in which is kept agitated by means of the bellows (A) during experimentation. An accurate thermometer may be included in the jacket to record the temperature of the water. The whole outfit is mounted on a wooden stand for convenience in manipulation (plate 1).

METHOD OF USE

The soil is weighed and placed in the portion (B_1) of the reaction bulb (fig. 2a) and the acid (HCl, 1:3), in the side tube (B_2). As only small amounts of the soil are taken for the experiments, extreme care should be exercised in the preparation of the sample. Attempts should be made to have a representative and perfectly pulverized preparation (1). Usually 40 borings are made in each twentieth-acre plot, the samples from alternate borings being composited to make the duplicate samples. The quantity of soil and also of acid will depend upon the amount of carbonate in the soil, but 1 to 2 gm. of soil and 3 ml. of dilute HCl have been found to be convenient. Only small amount of CO_2 should be allowed to be evolved, otherwise the gas may leak through the ground joint of the reaction bulb. With amounts up to 750 ml. there is absolutely no danger of leakage of CO_2. Anhydrous lanoline proved to be a suitable grease for the joints. When the side tube is being attached to the bulb it is advisable to apply 3 or 4 spots of the grease with a glass rod and then to press the side tube gently without rotating it. Under such circumstances the grease will flow uniformly over the ground surface, giving a thoroughly reliable joint. After the side tube has been fitted into the main part of the bulb (fig. 2a) the pressure inside the bulb is equilibrated with that of the air through the opening (O). Now the side tube is reversed, and a strong rubber band (R_2) is carefully applied (fig. 2b). As a result of this reversal, the acid is spilled into the main part of the bulb, which is now violently shaken with the long limb held in a horizontal position. After being shaken for 4 to 5 minutes, the bulb is worked onto the ground joint in the manometer and is secured by a rubber band (R_1). Now the taps (T_1) and (T_2) are opened, and the manometric liquid is adjusted to the zero mark on the manometric scale, when it should also stand at the mark (X) on the other limb. Subsequent to this adjustment, both the taps (T_1) and (T_2) are closed and the side tube (B_2) of the reaction bulb is again reversed (fig. 1). Because of the release of the compressed gas in the bulb, the liquid level in the graduated limb will be depressed below the zero mark on the scale. The Brodie solution is again adjusted to the mark (X), and the reading on the manometric scale is noted. The reading so obtained represents the increase in pressure, referred to as h in the formula, from which the amount of CO_2 evolved is easily computed. During experimentation the water in the jacket is kept stirred by means of the bellows (A).

EXPERIMENTAL

The accuracy of the apparatus was tested by liberating known volumes of CO_2 from bicarbonate solutions. The side tube received 0.2 ml. 0.05 N H_2SO_4 which was added to an excess of bicarbonate solution contained in the main

TABLE 1

Range of variability in CO_2 evolved by 0.2 ml. H_2SO_4 as measured by the apparatus

CO_2 EVOLVED IN μl. (N.T.P.)	DEVIATION FROM CALCULATED*	ERROR
		per cent
223.6	+1.0	0.45
220.4	−2.2	1.00
225.3	+2.7	1.25
222.0	−0.6	0.28
223.5	+0.9	0.40
224.5	+1.9	0.85
220.0	−2.6	1.20
221.5	−1.1	0.50
222.6	0	0
223.5	+0.9	0.40

* Calculated amount of CO_2 = 222.6 μl. at N.T.P.

TABLE 2

Range of variability in the carbonate content of a single sample as measured by the apparatus

CARBONATE CO_2	DEVIATION FROM MEAN	ERROR
per cent		*per cent*
0.209	−0.002	1.0
0.212	+0.001	0.5
0.212	+0.001	0.5
0.213	+0.002	1.0
0.209	−0.002	1.0
0.208	−0.003	1.5
0.214	+0.003	1.5
0.213	+0.002	1.0
0.215	+0.004	2.0
0.208	−0.003	1.5
0.207	−0.004	2.0
0.212	+0.001	0.5
0.207	−0.004	2.0
0.209	−0.002	1.0
0.210	−0.001	0.5

part of the reaction bulb. The gas space inside the bulb was filled with a gas mixture containing 95 per cent nitrogen and 5 per cent CO_2. In order to fill it with a suitable gas mixture, the bulb is first exhausted by means of a water pump until the pressure gauge indicates the required pressure, after which the gas mixture is allowed into it. The capillary of the manometer need not be

filled with any gas mixture, as the total volume of the gas inside it is negligible as compared to the volume of the total gas space. The values obtained for CO_2 evolved are presented in table 1. A glance at the values obtained will show that an accuracy of ± 1.25 per cent is easily obtainable in practice.

After the apparatus had been tested with bicarbonate solutions, some carbonate determinations in soils were made. In view of the great variations in carbonate content, it was thought advisable to make a number of determinations on a single sample of soil. The soil sample was obtained by digging a big hole to a depth of 1 foot and removing a uniform block of soil from the side. The soil was air-dried by placing it in a glass chamber, a current of air at 25–

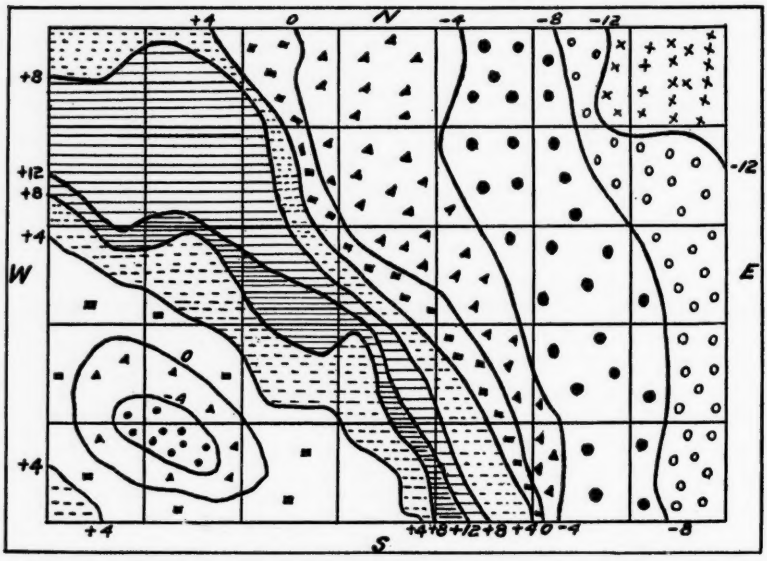


FIG. 3. CONTOUR MAP OF AN EXPERIMENTAL PLOT BASED ON THE CARBONATE CONTENT OF THE SOIL

30°C. being drawn over the soil by means of an electric fan. A mechanical analysis of the soil gave the following constituents: fine gravel, none; coarse sand, 0.7 per cent; medium sand, 0.6 per cent; fine sand, 1.8 per cent; very fine sand, 26.9 per cent; silt, 51.8 per cent; and clay, 18.2 per cent. One gram of air-dry soil was taken in the main part of the bulb while the side tube received 2.5 ml. dilute HCl. The values obtained for carbonate CO_2 are given in table 2. A point which emerged from this and other similar analyses is that considerable variations occur in the carbonate content of the soil even within short distances.

To get an idea of soil heterogeneity with regard to $CaCO_3$, 875 carbonate estimations were made on samples obtained from a piece of land 140 feet by

100 feet. This field was divided into 35 plots 20 feet by 20 feet, each of which was again subdivided into 25 subplots 4 feet by 4 feet each. Borings were made about the center of the ultimate plots, and the samples were analyzed for carbonate CO_2. The points at which the carbonate content was 4, 8, or 12 per cent below or above the mean value for the whole field were joined, and the contour map shown in figure 3 was constructed. Generally speaking, variations in the carbonate content may exist from one corner of the field to another corresponding roughly with the line of slope or as random patches of higher or lower carbonate content. From the topography of the field under observation it became evident that most of the variations in carbonate content could be attributed to the leaching action of water. The occurrence of random patches of higher or lower carbonate content suggested that considerable errors might be introduced in the results of varietal tests or in the response of varieties to different manurial treatments due to this type of soil heterogeneity.

SUMMARY

An apparatus for the estimation of carbonic acid in soils is described. In the construction of the apparatus, the use of rubber connections, which is likely to cause errors in various ways, has been avoided and an effective mixing of reactants rendered practicable. Because of its detachable nature, the reaction bulb is easily shaken by hand, and no shaking apparatus is required.

The accuracy of the apparatus, as found in practice, is ± 1.25 per cent.

A few experimental data are presented.

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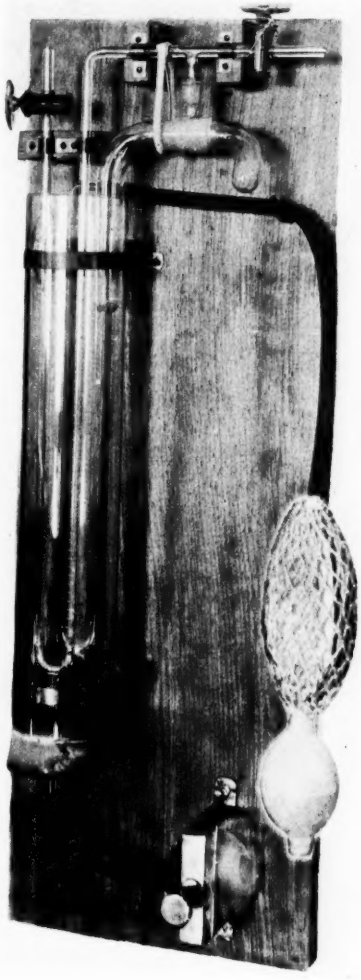
PLATE 1

APPARATUS FOR CARBONIC ACID ESTIMATIONS

PLATE 1



UNIV. OF MICH.

THE STATE IN WHICH THE HYGROSCOPIC MOISTURE EXISTS IN SOILS AS INDICATED BY ITS DETERMINATION WITH ALCOHOL[1]

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When air-dry soils are oven dried at 110°C. for 24 hours, a certain amount of water is driven off. It is not definitely known whether all this water exists in the soil as film or physically adsorbed water or whether part of it is also chemically combined or water of constitution. This uncertainty is especially true in the case of the organic portion of the soil.

It was thought that this question might be answered by determining the hygroscopic moisture of soils by means of alcohol. It was reasoned that if the moisture exists as physically adsorbed water or in the film form, the alcohol should extract or displace it. If, on the other hand, it exists as chemically combined water or water of constitution, the alcohol should not be able to extract or replace it.

In a former communication (1) it was shown that the total water content of soils can be accurately determined by means of methyl alcohol and a specially designed hydrometer. In that investigation it was found that the alcohol method agreed remarkably well with the oven-dry method in determining moisture content of soils. This agreement between the two methods would be a proof that all the water in the soil that is driven off at 110°C. exists in a physical form. In view of the fact, however, that the alcohol tends to dissolve some material from the soil, especially from the organic portion, and that this dissolved material affects the hydrometer reading in the same way as does water, it could not be concluded definitely that the alcohol takes out all the hygroscopic moisture. It was feared that any material dissolved by the alcohol might compensate for unextracted water.

In order to eliminate the difficulties presented by the hydrometer method, a reagent was required which would dissolve and separate the alcohol from the water and thus measure the water directly by volume. Such a reagent has been devised and patented by John F. Williams (2). It consists of a mixture of fusel oil, toluene, and tartaric acid. The fusel oil extracts the alcohol, the toluene prevents the fusel oil from retaining any water and separates and expels the water from the reagent, and the tartaric acid renders the reagent acid and

[1] Authorized for publication by the director as Journal Article 252 n.s. of the Michigan Agricultural Experiment Station.

thus prevents the formation of emulsions. When this reagent is mixed in a cylinder with ethyl alcohol containing water, two liquids separate out with a sharp line of demarcation between the two layers. The lower column of liquid is water, and the upper, a mixture of the other constituents. Actual tests have shown that this reagent will separate and determine the alcohol content of an ethyl alcohol-water solution within an accuracy of 0.5 per cent. With concentrations above 65 per cent alcohol the reagent does not work; such conconcentrations have to be diluted with distilled water. The presence of dissolved solids, except when the amount is rather large, does not affect the accuracy of the reagent.

To ascertain by the aid of this reagent whether or not the alcohol is capable of extracting all the hygroscopic moisture in soils and in some organic materials, the following procedure was devised. Into an Erlenmeyer flask were placed 50 gm. of air-dry soil and 50 cc. or more of 95 per cent ethyl alcohol. The flask was stoppered, and the mixture was allowed to stand for 24 hours with occasional shaking. The supernatant alcohol was then filtered and very accurately diluted with distilled water in the ratio of 1 to 1. Then 10 cc. of this liquid was taken by a 10-cc. pipette and placed in a special very narrow 25-cc. cylinder graduated into 0.1 cc. The cylinder was then filled with the reagent up to the 20-cc. mark, stoppered with a rubber stopper, and inverted seven or eight times to mix the reagent thoroughly with the alcohol solution. The cylinder was then set upon a table and allowed to stand for the water to separate from the mixture. At a temperature around 73°F. the separation of the water can be accomplished in about 10 minutes, but for certainty and high accuracy about 2 hours' time was always allowed for the separation. The volume of water so separated was carefully read and recorded. For basis of comparison or for ascertaining the exact amount of water that the alcohol extracted from the soil, a check was always run with the stock alcohol solution. This check test was performed exactly in the same way and at the same time as the test with the alcohol extract solution, and thus any error in the method was minimized or eliminated from the final experimental results. The difference in the volume of water between stock solution and the extract solution represents the amount of water contained in 10 cc. of each solution used. When this difference is multiplied by the total volume of alcohol employed to extract the soil, the total amount of water extracted by the alcohol from the soil is easily obtained. From the amount of soil used and the amount of water extracted from it, the percentage of water in the soil is readily calculated. This percentage of hygroscopic moisture as determined by the alcohol method is then compared with the percentage of hygroscopic moisture as determined by the oven-dry method in which the soil is dried at 110°C. for 24 hours.

The alcohol method as described has shown itself to be reliable and accurate, especially when checks are run parallel with the experimental tests and the tube is kept thoroughly clean and the temperature is above 70°F. At low temperatures the separation of the liquids is slow and frequently incomplete.

In table 1 are shown the percentages of hygroscopic moisture as determined by the alcohol method and by the oven-dry method in a number of typical mineral and organic soils.

The experimental data in table 1 show that in the case of the mineral soils the hygroscopic moisture as determined by the alcohol method is the same as that determined by the oven-dry method, indicating that the alcohol can extract or replace all the hygroscopic moisture. It will be noticed that the variation in the two methods is less than 1 per cent, which is considered to be within the experimental error. In the case of the mucks and peats, however, the oven-

TABLE 1

Comparison between alcohol method and oven-dry method in determining hygroscopic moisture in soils

MATERIALS	DEPTH	ALCOHOL METHOD	OVEN-DRY METHOD
	inches	*per cent*	*per cent*
Fuller's earth	....	9.2	10.0
Bentonite	....	10.57	11.31
Silica gel	....	1.40	1.04
Kaolin	....	1.20	1.16
McKenzie clay	B horizon	7.50	6.76
Grundy silt loam	Surface	2.50	2.74
Hagerstown clay loam	70–80	4.05	4.29
Hagerstown clay loam	12–70	2.90	2.81
Davidson clay loam	24–30	2.01	2.15
Greenville fine sandy loam	12–18	1.38	1.25
Decatur clay	0–6	1.20	1.32
Susquehanna clay	2–6	3.72	3.98
Lufkin clay	10–16	9.35	10.22
Colby silt loam	subsoil	1.74	1.85
Fargo clay loam	6–16	5.38	5.23
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	.....	0.00	37.8
Muck 1	.....	10.1	15.2
Muck 2	.....	10.66	15.7
Muck 3	.....	9.17	16.2
Peat 1	.....	9.00	13.35
Peat 2	.....	9.98	15.02
Wheat flour	.....	8.82	12.80

dry method gives about 5 per cent more moisture than the alcohol method, indicating either that the alcohol is unable to extract all the hygroscopic moisture or that the oven-dry method causes these organic materials to undergo partial decomposition which is revealed as hygroscopic moisture. The latter hypothesis is probably the correct one, inasmuch as the alcohol is able to extract the hygroscopic moisture of such materials as silica gel, fuller's earth, and bentonite, and the nature of the organic materials is such that some decomposition might be expected to take place at the temperature of 105–110°C.

All evidence obtained in the course of the present investigation indicates

that the data in table 1 are reliable and accurate. One of the strongest evidences that such is the case is afforded by the results in table 2, which show that after bentonite, fuller's earth, and various soils have been dried at 110°C. for 24 hours alcohol extracts no water or anything else which affects the reading, and yet when these materials are in air-dry condition considerable amounts of water are extracted.

The facts revealed in the experimental data in table 1 are of fundamental importance. They indicate (*a*) that the hygroscopic moisture in the mineral soils probably all exists as physically adsorbed or film water; (*b*) that even though this film water is held with enormous forces, is greatly compressed, and can be expelled only at a temperature of 110°C. for several hours, yet the alcohol is able to extract it readily in only a few minutes; (*c*) that in the case of the organic materials a considerable part of the loss on heating at 105°–110°C. may represent volatilization and water of decomposition and not hygroscopic moisture; (*d*) that the method previously offered (1) to determine the moisture

TABLE 2

Amount of water extracted by alcohol from soils in oven-dry and air-dry condition

SOILS	OVEN-DRY SOILS	AIR-DRY SOILS	MOISTURE DETERMINED BY OVEN-DRY METHOD IN AIR-DRY SOILS
	per cent	*per cent*	*per cent*
Bentonite	0.0	10.57	11.31
Fuller's earth	0.0	9.20	10.00
Muck	0.0	10.20	15.2
Clay	0.0	7.50	6.76
Loam	0.0	4.05	4.29

content of soils by means of alcohol and a hydrometer is sound in principle and reliable.

Attention must be directed to the results (table 1) obtained with copper sulfate, a hydrate which is insoluble in alcohol. It will be seen that this copper sulfate contained 37.8 per cent water, according to the oven-dry method, and yet the alcohol failed entirely to extract any of this water. These results are suggestive and significant as to the different forms of water which may exist in the materials.

SUMMARY

Hitherto it has not been definitely known whether the hygroscopic moisture of soils, which is driven off by heating at 110°C., exists exclusively as film or physically adsorbed water or partly as chemically combined water.

An attempt has been made to throw light upon this question by extracting soils with alcohol and then determining the quantity of water found in the alcoholic extract. By means of a special reagent consisting of fusel oil, toluene,

and tartaric acid, the water extracted by the alcohol can be determined volumetrically.

It was found that in the case of mineral soils, the alcohol extracts all the hygroscopic water, indicating that the hygroscopic moisture in mineral soils exists entirely in the form of physically adsorbed or film water.

In the case of mucks and peats and some other organic materials studied, the alcohol extracts about one third less water than is indicated by the oven-dry method. The explanation for this is that either the alcohol is unable to extract all the water from the organic materials or the oven-dry method causes these organic materials to undergo partial decomposition or volatilization of substances other than water, with consequent high and erroneous values for hygroscopic water. The latter seems the more likely possibility.

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THE INFLUENCE OF THE REACTION OF SOIL STRATA UPON THE ROOT DEVELOPMENT OF ALFALFA[1]

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Failure in the growth of alfalfa is experienced in many cases in the eastern part of the United States where apparently good stands and growth should be obtained, if one judges from cultural practices. In some instances where rather acid soils have been recently limed for the first time, it is observed that good stands are obtained, but the yield is low the second year and the alfalfa "runs out" quickly. Inspection of some of these cases reveals a shallow rooting system. In other instances it is noticed that soils of a similar nature which have been continuously and systematically limed over a long period of years produce good crops.

These observations have led to the study of the reaction of soil strata upon the root development of alfalfa.

PLAN OF EXPERIMENT

The alfalfa in this experiment was grown at the Pennsylvania State College in 52 sewer tile, 15 inches in diameter and 24 inches in depth, placed in the ground up to the flange. Care was taken to provide good drainage, and clover was planted around the tile for protective purposes. The various treatments were made in replicas of six to allow a set of two to be removed in consecutive years.

Soil used

The soil used was a virgin Dekalb silt loam surface soil obtained from the Pennsylvania Experiment Station substation at Snowshoe. None of the A_0 horizon was used. The pH value (quinhydrone) was 4.7.

Treatments

Two main treatments of one-half lime requirement and full lime requirement were made to the surface 3 inches of soil. Each of these treatments had sub-layer treatments of no lime, one-fourth lime requirement, and one-half lime

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[2] Associate professor of agronomy, New Mexico College of Agriculture & Mechanic Arts, State College, New Mexico. The author is deeply indebted to Dr. A. L. Patrick and Prof. F. D. Gardner of Pennsylvania State College for many helpful criticisms and suggestions regarding this paper.

requirement. In addition, one set received one-half lime requirement to the depth of 6 inches with no lime to the sublayer, and one set had no lime added to either layer.

In all cases muriate of potash and superphosphate were added to the upper 3 inches of soil *at the rate* of 100 pounds and 600 pounds respectively, to the million pounds of soil. The various treatments, including the calcium carbonate treatment, are shown in the following tabulation.

LIME TREATMENT*		$CaCO_3$ PER 1,000,000 POUNDS MOIST SOIL	
0"–3"	3"–24"	0–3"	3"–24"
		pounds	*pounds*
0 L	0 L	.....	.....
1/2 L	0 L	1,000	.....
1/2 L	1/4 L	1,000	500
1/2 L	1/2 L	1,000	1,000
1 L	0 L	2,000	.....
1 L	1/4 L	2,000	.....
1 L	1/2 L	2,000	1,000
1/2 L†	0 L	1,000	.....

* 0 L = No lime.
1/4 L = 1/4 lime requirement.
1/2 L = 1/2 lime requirement.
1 L = Full lime requirement.
† Limed six inches deep.

The lime applied was in the form of calcium carbonate testing 96 per cent $CaCO_3$ and 1 per cent $MgCO_3$, 85 per cent passing through a 100-mesh sieve and all through a 30-mesh sieve.

The lime requirement was determined by replacement of the hydrogen with a normal $BaCl_2$ solution and titrating with NaOH.

Cultural data

Grimm alfalfa was inoculated with an especially hardy strain of *Bac. radicicola*. The alfalfa was thinned each year to the ten best plants. It was planned to permit the alfalfa to grow over a 2-year period, but winter killing necessitated replanting of the remaining tile the second spring. On the third series of tile this second year's planting was allowed to remain until the following spring of 1930.

The cultural record is as follows:

OPERATION	1928	1929
Put soil in tile	May 12–19	
Planted alfalfa	May 31	May 27
Sampled for replaceable Ca	Sept. 27	Aug. 11
Harvested tops	Oct. 1–11	Aug. 12–18
Removed roots	Oct. 1–11	Aug. 12–18

SOIL CONDITIONS DURING THE EXPERIMENT

Hydrogen-ion concentration

The hydrogen-ion concentration of the surface soil for the unlimed tile was about 4.8 (quinhydrone) throughout the experiment; for the treatment receiving 1000 pounds of limestone to 1,000,000 pounds of soil, about 5.6; and for the surface soil receiving 2000 pounds of limestone to 1,000,000 pounds of soil, 6.3.

After the limestone was added May 12 to 19, 1928, the pH values of all the tile reached their highest value in the July 22, 1928, sampling (fig. 1). A slight decrease in pH value took place throughout the remainder of the season. In 1929 the pH value of the surface 3 inches on April 27 was slightly higher than on the preceding October. As in 1928, there was a slight decrease in pH as the season progressed. On the whole, the pH value of the surface soil for each treatment was lower the second year than the first year. This difference, however, was not great.

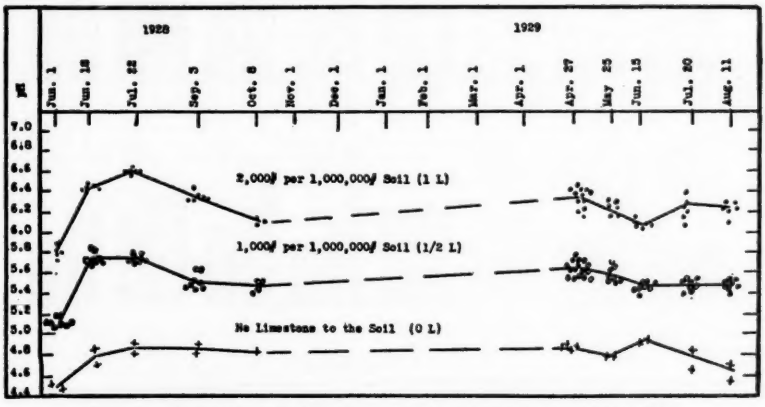

FIG. 1. pH OF SURFACE 3 INCHES THROUGHOUT SEASONS 1928–1929

A comparison of the pH values between years (fig. 2) in the various soil layers taken at the end of each season shows, in general, an essential similarity. A slight raise in pH value occurred in the second year in the 6- to 12- inch layer and possibly a slight lowering, in general, of pH in the first and second 3-inch layers. This change between years, however, in the most extreme case between different tile of the same treatments, was only a pH of 0.34 and, in the majority of cases, was less than 0.2 pH, which is within experimental error. Accordingly, a discussion of the average of the two years is all that is necessary at this place.

The soil in the tile receiving no lime treatment to either the surface or sublayer had nearly the same pH value for both the upper and second 3 inches (pH 4.7).

The pH of the second 3 inches of the limestone treated tile, however, shows that it was affected by the quantity of limestone applied to the surface 3 inches

as well as that applied to the sublayer. Also, the higher quantities of limestone added to the various sublayers augmented this change. In general, the pH for the second 3 inches for the two years was half way between the pH values of the surface layer and the sublayer lying below the depth of 6 inches. The pH of the unlimed sublayer below the depth of 6 inches was about 4.7, or the same as that for the tile receiving no limestone in the entire soil column. For the sublayer below 6 inches receiving 500 pounds of limestone ($\frac{1}{4}$ L) the pH averaged 5.1, and for that receiving 1000 pounds of limestone, pH of 5.6, or the same as the surface 3 inches with the same treatment.

These results show that the surface treatment decreased the acidity of the second 3 inches to some extent and possibly a very small amount of the second 6 inches over a 2-year period.

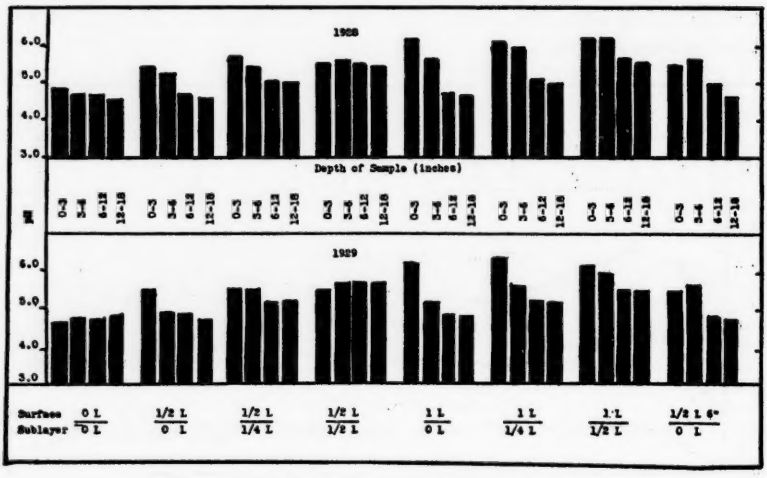

FIG. 2. pH OF THE SOIL AT THE DIFFERENT DEPTHS

Replaceable calcium

One of the outstanding results of the experiment is the close correlation between replaceable calcium and the hydrogen-ion concentration.

At the end of the first season the correlation coefficient between replaceable calcium at the various soil depths and the pH was 0.974 ± 0.00433. At the end of the second season it was 0.923 ± 0.01346. The correlation using all the values for both years was 0.856 ± 0.0165.

The replaceable bases were extracted with 0.1 *N* HCl, which may account partly for the poorer correlation when the two years are taken together. No doubt some of the calcium analyzed the end of the first season as replaceable was not strictly replaceable but came from $CaCO_3$ remaining in the soil from the original application. Also, the surface 3 inches of all the tile received an application of 600 pounds of 16 per cent superphosphate to 1,000,000 pounds of soil,

which, especially the first year, is reflected in the exchangeable calcium in this layer.

Since there is so high a correlation between pH and replaceable calcium for each of the various depths at which the samples were taken, it is not surprising to find that the soil conditions in regard to replaceable calcium parallel those already discussed for pH (fig. 3).

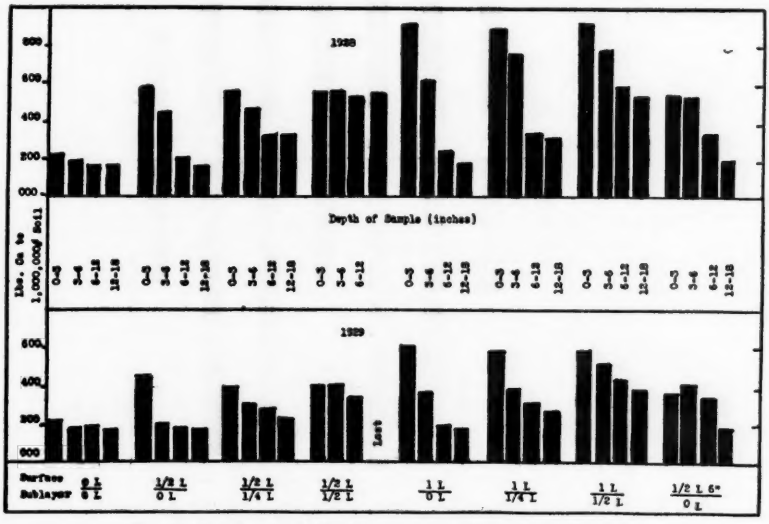

FIG. 3. REPLACEABLE CALCIUM AT THE DIFFERENT DEPTHS

THE RELATIONSHIP OF YIELD AND ROOT LENGTH TO pH AND REPLACEABLE Ca

Although the 1929 growing season was not so favorable, especially in regard to moisture penetration, for the growth of alfalfa as the 1928, and although fertilizers were not added the second year, the results of each year were essentially the same in regard to root action as affected by the pH of the soil layers (figs. 4 and 5).

The various treatments of the surface and sublayers of the soil decidedly influenced the yields of tops and the penetrations of the roots. In addition, the various liming treatments of the surface 3 inches influenced the yields of the tops.

Little or no root growth was found in soil of a pH of 4.7, which was that of the virgin soil. When the pH of the soil was raised to 5.0 or above, either through the direct addition of lime to the soils or through the movement of calcium into the lower layer, root development took place in that layer. An average of the two years' results indicates that the more vigorous root development was found in the soil as the pH approached neutrality (fig. 6).

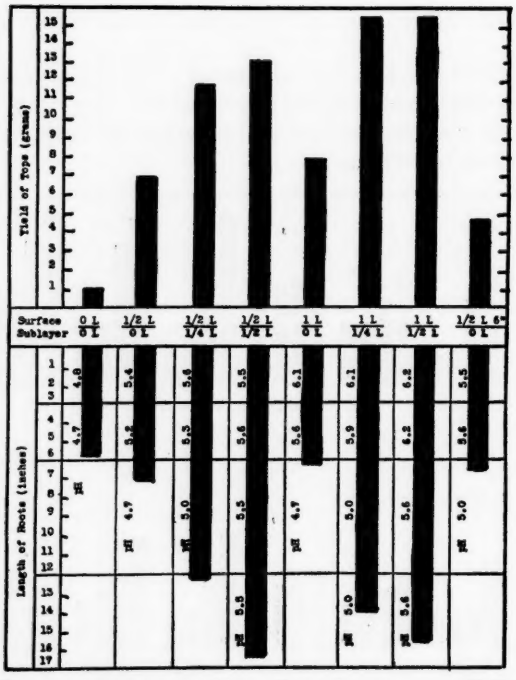

FIG. 4. RELATIONSHIP BETWEEN YIELD, ROOT GROWTH, AND pH VALUE, 1928

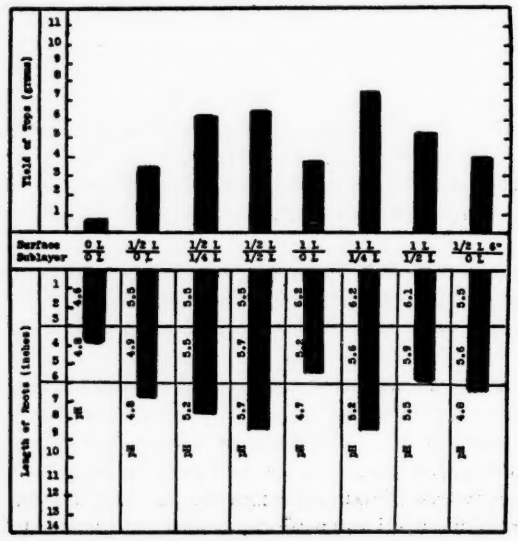

FIG. 5. RELATIONSHIP BETWEEN YIELD, ROOT GROWTH, AND pH VALUE, 1929

The yield of tops was in direct relationship to the length and vigor of root growth. In general, the yields of tops were greater where the root penetration was the deepest. Where the pH of the soil was raised to 6.2 in the surface 3 inches, the yield of tops was increased over that of those plants growing in the soils with the surface 3 inches at a pH around 5.5. The soils on which the pH of the surface 3 inches had been raised to 6.2 by limestone also had a higher pH value in the second 3 inches as compared with similar sublayer treatments of smaller surface lime applications.

The application of lime to the depth of 6 inches with none to the sublayer gave no better results than where lime had been applied to only the surface 3 inches. The second 3 inches of this latter treatment, however, had a pH of 5.0

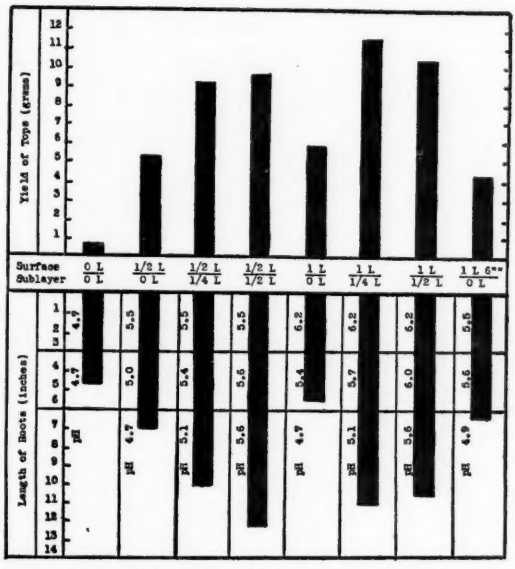

FIG. 6. RELATIONSHIP BETWEEN YIELD, ROOT GROWTH, AND pH VALUE, AVERAGE 1928–1929

whereas the pH on both treatments below 6 inches was under 5.0. The second season, however, was proportionally better with this treatment than was the first.

Nodulation

Nodulation on the plants was good in all the surface soils which received liming. The plants in the tile receiving no lime had only an occasional nodule. Roots in the sublayers receiving no lime under the limed surface layer were fairly well noduled; where the sublayer had been limed, nodulation was good (table 1).

TABLE 1

Nodulation of roots at different depths for various treatments

TREATMENT		1928		1929	
Surface	Sublayer	0–3″	3–6″	0–3″	3–6″
0 L	0 L	Poor	Poor	Poor	Poor
1/2 L	0 L	Medium	Fair	Fair	Fair
1/2 L	1/4 L	Good	Medium	Medium	Medium
1/2 L	1/2 L	Medium	Medium	Good	Medium
1 L	0 L	Good	Poor	Good	Medium
1 L	1/4 L	Good	Medium	Medium	Medium
1 L	1/2 L	Good	Good	Good	Medium
1/2 L 6″	0 L	Medium	Medium	Good	Good

TABLE 2

Conditions of plants in tile after winter of 1929–30

TREATMENT		TILE NUMBER	NUMBER OF PLANTS		CONDITION
Surface	Sublayer		Fall December 20, 1929	Spring June 7, 1930	
0 L	0 L	C10	4	4	Very small
		D12	10	6	Very small
1/2 L	0 L	A9	4	4	Small
		B11	8	8	Small
1/2 L	1/4 L	B9	11	11	Fair
		C11	7	7	Fair
1/2 L	1/2 L	C9	10	10	Good
		D11	12	9	Good
1 L	0 L	C13	8	8	Fair
		D9	10	10	Fair
1 L	1/4 L	A10	8	8	Fair
		D13	8	8	Fair
1 L	1/2 L	B10	7	7	Good
		C12	12	7	Good
1/2 L 6″	0 L	A11	8	8	Fair
		D10	9	9	Fair

Vigor of the plants the second spring

The first year the plants were all winterkilled, but the second year planting did not fare so badly, no winterkilling being noticed after the winter of 1929–30.

The growth on the tile receiving no limestone was very poor the spring of 1930. That receiving only 1000 pounds to the surface and none below 3 inches also showed poor growths. The tile receiving 1000 pounds and 2000 pounds to the surface and 500 pounds to the sublayer showed fair growth. Tile having 2000 pounds and 1000 pounds added to the surface 3 inches per acre and 1000 pounds to the sublayer showed good vigor in the spring (table 2).

DISCUSSION

The results show that under the conditions of the experiment root growth was meager in the soil layers at a pH under 5.0, but that upon addition of lime to bring the pH to 5.5 and 6.2 good root penetration and subsequently good yields of tops were obtained. The results further show that applications of lime raise the pH and replaceable calcium in the immediate sublayer soon after addition of the limestone, which in turn influences the root growth.

The poor growth in soil layers having a pH of less than 5.0 may be attributed to one or a combination of the following factors: deficient nutrient supply, aluminum toxicity, high hydrogen-ion concentration.

Deficient nutrient supply

In this experiment, if root growth had been just poor or nominally weak in the layer receiving no lime, there might have been a question of the effect of nutrient supply on root development. The root growth in this experiment, however, was unusually weak, if not almost entirely inhibited, in the soil layers which received no lime. That sufficient food nutrients are present for general growth is shown by the natural vegetation on the soil in its native state.

Although Weaver, Jean, and Christ's (17) experiments show that where roots come in contact with a fertilized layer of soil they developed more abundantly, branched more freely, and the presence of such a layer seemed to retard normal root penetration into the soil below, they did not say it inhibited root growth in the other layers.

On the other hand, the works of Wolters (21) with cane, Lees (10) with wheat, and Davis (4) with alfalfa show that under normal conditions the roots of plants receiving fertilizers penetrated deeper than those receiving no fertilizers.

The work of Weller (18) with roots of cane in root study boxes with fertilizers applied to various parts of the root system is also of interest here. His results show that stimulation of the entire root system as well as a local stimulation was found to be the case.

Gile and Carreo (7) with different nutrient solutions of nitrogen, phosphorous, and potassium confined to separate roots showed that there is an unusual transference of nitrogen to the roots in phosphorous and potassium solutions and an extraordinary transference of phosphorous to the roots in the

nitrogen and potassium solutions. With other solutions which might represent the conditions of this experiment, they found the following:

TREATMENT		GRAMS PER ROOT	
Flask A	Flask B	Flask A	Flask B
N P K	O	0.0455	0.0267
N P K	K	0.0302	0.0205

The flasks, of course, contained the other necessary nutrients.

In considering separate nutrients, Brenchley (2) has shown that a provision of phosphates for the first 6 weeks allowed normal growth to take place in grain. Gericke (6) obtained a maximum dry weight with wheat when the plants were grown in the nutrient solution for 4 weeks and were then transferred to solutions containing no phosphate. The continuance of growth of the roots in these experiments shows that phosphorous is transferred to the root from one part to another.

Truog (16) further shows that "solid phase" feeding probably takes place in plant nutrition, especially with phosphorous. A pH of 4.7 or aluminum and iron phosphate should not interfere entirely with phosphorous assimilation. Furthermore, available phosphorous is never found except in traces in Dekalb soil such as was used in the experiment reported here. Still a good growth was obtained in the sublayers which received no phosphorous but were limed.

From this review of literature and the results obtained in the experiment reported in this paper, it is believed that the plants received sufficient phosphorous for root penetration in the soil layers with a pH below 5.0.

It has been thought by some that lack of calcium for nutritional purposes might account for the decrease in yield of alfalfa on soil low in calcium, but this will not account for lack of root penetration if we concede that calcium absorbed by one part of the root system is available to other parts of the root system, as is apparently the case with phosphorous. Also, it will be remembered that although the roots showed very good growth in the upper limed layer, they did not penetrate into the lower layer with a pH of 4.7.

Duley (5) reports that where the soil contained 553 pounds of calcium per acre soluble in 0.04 *N* carbonated water, liming was profitable, whereas where 810 pounds were soluble, only small returns from liming were obtained. Along this same line Whitson, Chapman, and Hull (19) found that with the extraction of calcium with 0.04 *N* carbon dioxide solution, soils showing but 346 pounds to the acre produced poor alfalfa whereas soils with 565 pounds produced good alfalfa. These results show that calcium as a food supply may be a limiting factor in growth.

The experiment conducted here, however, shows that representative soil

layers with varying pH values had the following amounts of 0.1 *N* HCl extracted calcium to 2,000,000 pounds of soil:

pH	*Pounds of 0.1 N HCl extracted calcium*
4.7	380
5.2	926
5.4	1,096
5.8	1,476
6.2	1,565

No doubt 0.1 *N* HCl extraction and 0.04 *N* carbonated water extraction are not comparable; however, judging from the root growth in the various horizons, the soil with a pH above 5 had sufficient calcium for plant growth. Under the conditions of this experiment the layers with a pH of 4.7 where little root growth took place had, perhaps, close to the limiting point of available calcium for plant growth. With large mature plants in this soil, calcium might have been a limiting factor if the plant had grown to this extent in the unlimed soil, but it is felt that at a pH of below 5.0 some factor other than calcium was the limiting factor. At a pH of above 5.0, where plant growth was more nearly normal, indications are that calcium might have been a limiting factor with the smaller lime treatments.

In regard to nitrogen, Karraker (9) noted that nodulation was correlated with soil reaction fully as well when a particular reaction affected only a part of the roots of a plant as when it affected the entire root system.

According to this, if the reaction is proper in one part of the soil, good nodulation will take place. This experiment shows that in the limed layers good nodulation took place. Although, no doubt, good nodulation influenced the yield, it did not cause or prevent root penetration. There was only an occasional nodule found below 6 inches in any of the tile; yet, where conditions were favorable, root penetration was below this depth.

Aluminum toxicity

Aluminum toxicity has been advanced by Blair and Prince (1), Skeen (15), McLean and Gilbert (11), and others as one of the controlling factors in limiting plant growth at low pH values.

Magistad (12) presents water culture data to show that at acidities greater than a pH of 5.0 all the crops tried, except alfalfa, suffered both strong aluminum toxicity and strong H-ion toxicity; however, alfalfa died whether aluminum was added or not, showing that a pH of under 5.0 is definitely detrimental to alfalfa. His results also show no aluminum toxicity toward alfalfa with pH values above 5.0. Although it is almost impossible to differentiate between aluminum toxicity and hydrogen-ion toxicity, this work of Magistad would indicate that aluminum is not necessarily the limiting factor with the experiment reported here.

High hydrogen-ion concentration

As just stated, it is difficult to separate aluminum and hydrogen-ion toxicity or the subsequent resulting effects from their ionic concentration; however, it is thought that the lack of penetration of the roots in this experiment was due primarily to hydrogen-ion concentration.

Joffe (8) showed that the germination of alfalfa seed was practically the same with pH values of soil varying from 4.5 to 7.0 but was greatly reduced in cultures which yielded soil extracts having pH values below 4.5. Yields of alfalfa tops showed a gradual increase with an increase in the pH values of soil extracts from 3.8 to 7.0. Bryan (3) showed that alfalfa will not establish itself at a pH of 4.0 and produced its maximum growth at a pH of 7.0 and 8.0. Sewell and Gainey (14) conclude that the reaction of the soil, if within a range of pH 4.5 to 7.0, is a minor factor affecting growth of alfalfa if all the needed nutrients are supplied. Magistad (12) found that alfalfa suffered greatly at a pH of 5.0.

Results of the tile experiment show decidedly that good root growth was not obtained in soil under the conditions of the experiment at a pH of 4.7.

In summarizing the cause of the behavior of the roots to the various soil reactions, it would seem that below a pH of 5.0 the hydrogen-ion concentration has a direct effect on the roots in inhibiting growth and therefore good penetration. Where the pH is raised above a pH of 5.0, no doubt other factors enter in to promote better root development. This is probably due to the increased amount of calcium for plant nutritional purposes and increased biological activities brought about by higher pH values. This is shown by the increased vigor of the plants and roots of the experiment as the pH approached more nearly the neutral point.

The results also show that surface liming, by its influence on the substrata, will increase root penetration. That surface application of lime will change the reaction of the substrata is now well established. Nelson (13) and Wilson (20) have shown this to be the case. Analyses made by the writer on virgin soil and limed soil throughout the state of Pennsylvania also have shown this to be true. The amount of change, however, will depend on the rate of application and the length of the liming practice.

The experiments reported in this paper show that the pH of the second 3 inches of soil immediately below the limed strata is materially raised, and, over a 2-year period with moderate liming, possibly the pH of the strata below this may be raised slightly. It is also seen that where such changes have occurred in the pH value in the sublayer root penetration is obtained.

SUMMARY

The experiment reported here was conducted with alfalfa grown on a Dekalb silt loam surface soil placed in large sewer tile. The surface and sublayers of the soil were treated with varying quantities of limestone.

The pH value of the surface soil varied with the season to some extent and

on the limestone treated tile was slightly lower on an average the second year than the first.

The pH and replaceable calcium by 0.1 *N* HCl extraction had a correlation of 0.856 ± 0.0165 over the period of two seasons.

The pH values of the sublayers were influenced materially by the calcium carbonate additions to the layers above, the amount depending on both the quantity of limestone added to the upper layer and that added to the lower layer. The depth of effect on pH in the sublayer depended also to some extent on length of liming history.

Root development correlated definitely with the pH and with the replaceable calcium of the various soil layers. A pH of 4.8 checked root growth almost entirely; a pH slightly above this, retarded root growth. The roots grew well in a pH above 5.

Depth of root penetration is definitely correlated with the yield of alfalfa, under the conditions of this experiment.

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PLATE 1

EFFECT OF DIFFERENT LIMESTONE TREATMENTS OF SOIL ON GROWTH AND ROOT DEVELOPMENT OF ALFALFA

FIG. 1. No limestone.

FIG. 2. Surface 3 inches, full lime requirement; sublayer, no lime.

FIG. 3. Surface 3 inches, full lime requirement; sublayer, one-fourth lime requirement.

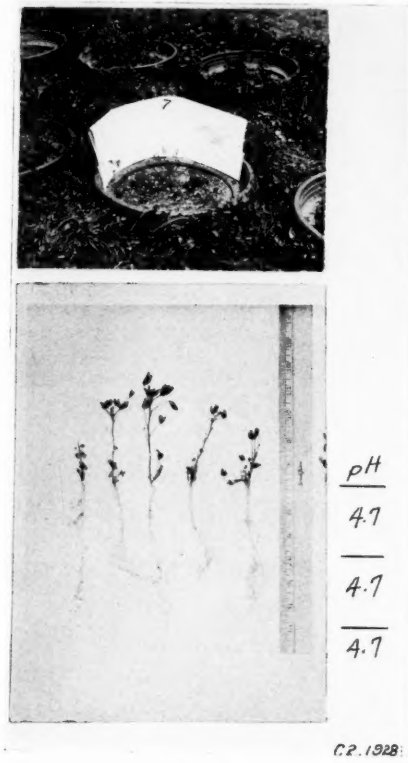

FIG. 1

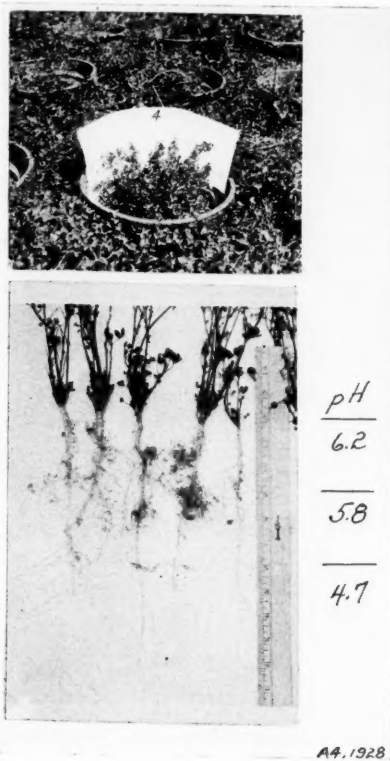

FIG. 2

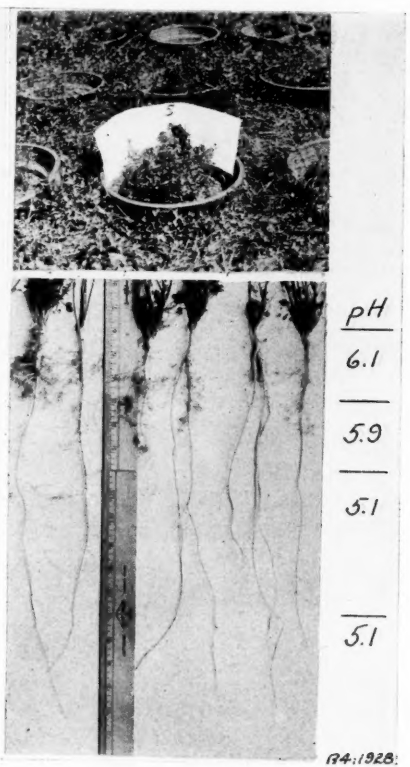

FIG. 3

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PLATE 2

EFFECT OF DIFFERENT LIMESTONE TREATMENTS OF SOIL ON GROWTH AND ROOT DEVELOPMENT OF ALFALFA

FIG. 1. Surface 3 inches, full lime requirement; sublayer, one-half lime requirement.
FIG. 2. Surface 3 inches, one-half lime requirement; sublayer, no lime.
FIG. 3. Surface 3 inches, one-half lime requirement; sublayer, one-fourth lime requirement.

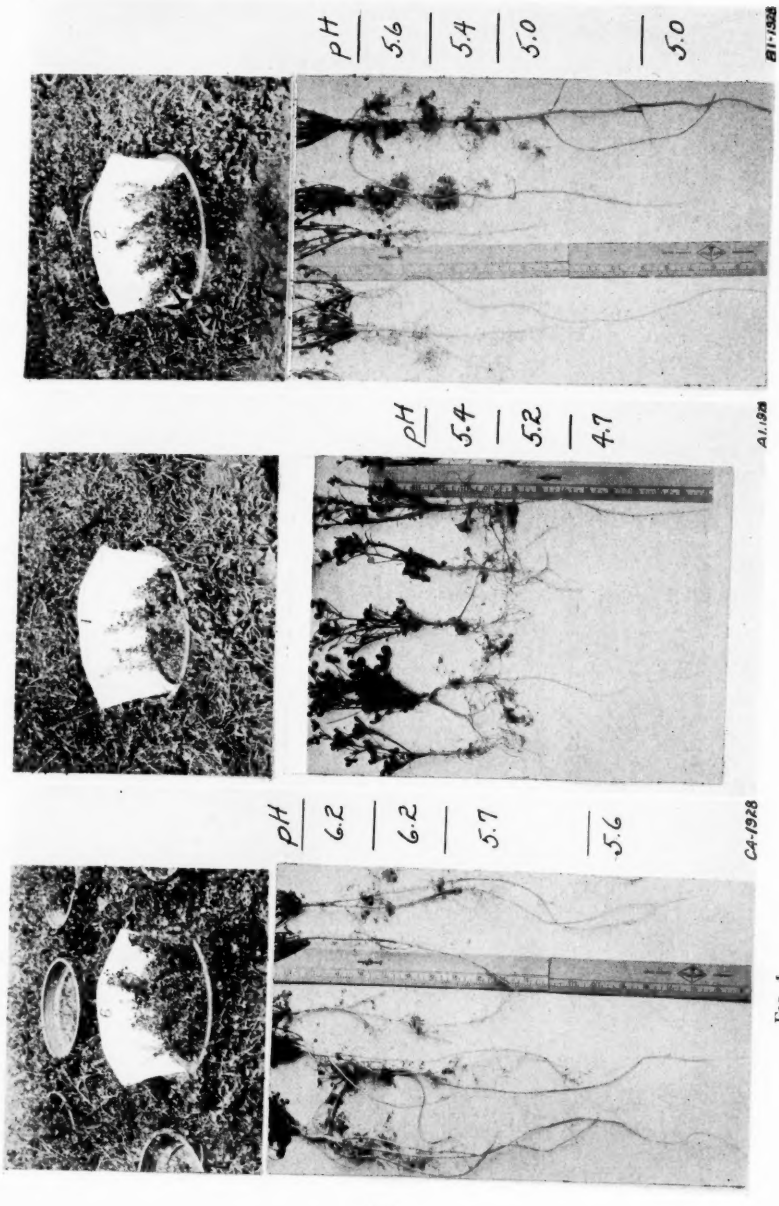

FIG. 1

FIG. 2

FIG. 3

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PLATE 3

EFFECT OF DIFFERENT LIMESTONE TREATMENTS OF SOIL ON GROWTH AND ROOT DEVELOPMENT OF ALFALFA

FIG. 1. One-half lime requirement.

FIG. 2. Surface 6 inches, one-half lime requirement; sublayer, no lime.

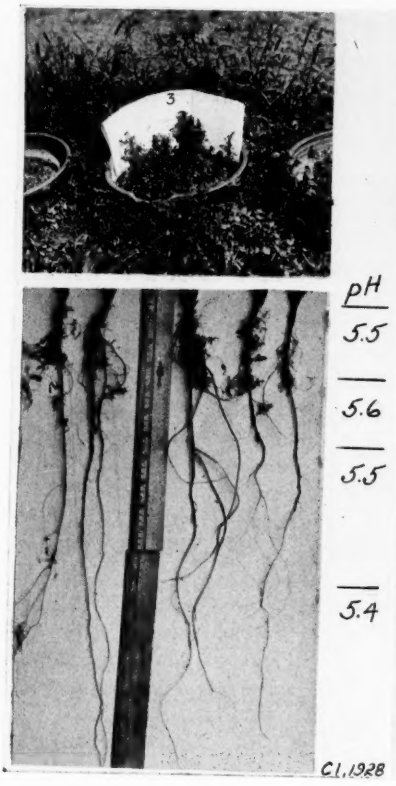

FIG. 1

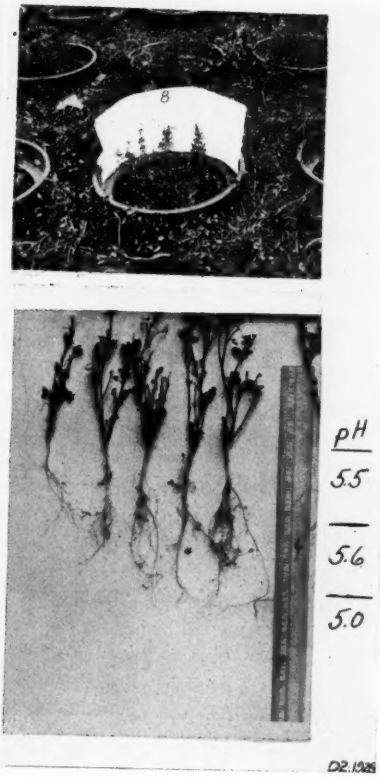

FIG. 2

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NUTRITION STUDIES WITH CORN: I. A STATISTICAL INTERPRETATION OF THE NUTRIENT ION EFFECT UPON GROWTH IN ARTIFICIAL CULTURE[1]

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The purpose of these experiments is to test a somewhat different method of approach in the interpretation of physiological balance studies in relation to plant growth.

Since the adoption by Tottingham (9) of a system of graphical representation in the study of physiological balance, the idea of controlled variation of plant nutrients in the growth medium has been further developed and utilized in various ways. The historical background prior to 1914 is thoroughly summarized by Tottingham in a paper presenting the four-salt, pyramidal system for nutritional study (9). In 1915, Shive presented his triangular system, combining into three-salt solutions (8) the six major ions most commonly used in nutritional work. Jones and Shive (5) modified Tottingham's four-salt solution, replacing the KNO_3 with $(NH_4)_2SO_4$, for purposes of comparing the influence of the nitrate ion, NO_3^-, with that of the ammonium ion, NH_4^+.

Livingston and Tottingham (7), in 1918, numbered and catalogued the six possible three-salt solutions which can supply the six major ions. Johnston (4), Gericke (3), and others, by working with these six types of solutions, were able to bring out some of the metabolic relationships of the various ions by comparisons among the types.

The simplicity of the three-salt solution makes it a valuable tool for many types of research, but any such solutions have the obvious disadvantage that if the proportion of one ion of a salt is altered, the accompanying ion of the salt must be varied in like proportion. For this reason, a system in which the relative concentration of each ion could be varied separately should greatly simplify the interpretation of the physiological significance of that ion.

CALCULATION OF THE SOLUTIONS

In order to create a system in which the concentration of any one ion may be varied as desired with that of any other ion, all nine of the salts used by Livingston and Tottingham are needed. This would require a vastly more intricate

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of plant physiology.

system, provided that some other means of simplification were not introduced. In order to effect this simplification, it was decided to use each ion at only three concentrations, i.e., corresponding to three multiples of the one-tenth increment of the total concentration.

The solutions were devised directly from the triangle of Shive (8), using the solutions represented by the three apexes and one centrally located point, R_3C_3, as bases for computations and comparisons. Figure 1 is a reproduction of Shive's triangle, with the four numbered solutions of this series indicating

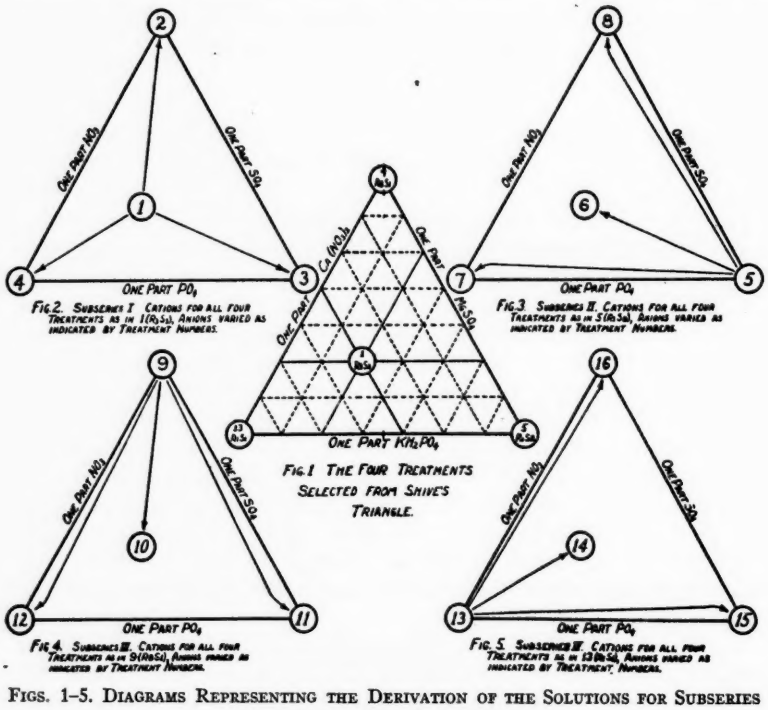

FIG. 2. SUBSERIES I. CATIONS FOR ALL FOUR TREATMENTS AS IN 1(R_3S_3). ANIONS VARIED AS INDICATED BY TREATMENT NUMBERS.

FIG. 3. SUBSERIES II. CATIONS FOR ALL FOUR TREATMENTS AS IN 5(R_3S_3). ANIONS VARIED AS INDICATED BY TREATMENT NUMBERS.

FIG. 1. THE FOUR TREATMENTS SELECTED FROM SHIVE'S TRIANGLE.

FIG. 4. SUBSERIES III. CATIONS FOR ALL FOUR TREATMENTS AS IN 9(R_3S_3). ANIONS VARIED AS INDICATED BY TREATMENT NUMBERS.

FIG. 5. SUBSERIES IV. CATIONS FOR ALL FOUR TREATMENTS AS IN 13(R_3S_3). ANIONS VARIED AS INDICATED BY TREATMENT NUMBERS.

FIGS. 1–5. DIAGRAMS REPRESENTING THE DERIVATION OF THE SOLUTIONS FOR SUBSERIES 1 TO 4 FROM SHIVE'S TRIANGLE

the focal points selected. From each of these focal points, the concentration of anions was varied with each of the other points, with the cations held constant. For example, there were four distinct solutions employed in which the cations were maintained in the same proportion as in Shive's R_3C_3, but the anions were present in four different proportions which correspond to Shive's R_8C_1, R_1C_8, R_1C_1, and R_3C_3. This manipulation is indicated in figure 2. Similarly, figure 3 represents the four solutions in which the cations were supplied in the ratio of R_1C_8 and the anions varied as previously mentioned. Solutions in which the cation ratios were maintained as in R_8C_1 and in R_1C_1 are indicated

by figures 4 and 5, respectively. This manipulation of the anions and cations separately was accomplished by the use of nine salts, as already mentioned. Such an arrangement gives four subseries of four treatments each, as is indicated in the diagrams. A similar arrangement, wherein the cation concentration is varied to each of the focal points while the anion concentration is held constant, gives four further subseries, but these, which will be considered as subseries 5–8, are merely rearrangements of the same 16 treatments.

It is impossible to control absolutely either the osmotic proportions or the chemically equivalent proportions of the ions used in varying the ionic concentrations for the various solutions. Valence differences of the ions and differences in the ionization constants of the salts do not, however, prevent close approximations of the calculated ionic proportions.

In preparing these solutions, the procedure has been first to ascertain the multiples of the osmotic increment (one-tenth in this case) and the corresponding partial volume-molecular concentrations of the three salts which would be present in a solution of the stipulated cation proportion. Thus, for a solution with cations in the R_3C_3 ratio at 0.5 atmosphere concentration, these would be:

Salt	*No. of increments*	*Volume molecular*
KH_2PO_4	3	.0031
$Ca(NO_3)_2$	3	.00225
$MgSO_4$	4	.0057

Next, the multiples of the osmotic increment and the corresponding partial volume-molecular concentrations of the three salts which would be present in a solution of a given anion proportion are considered. If the anions should be in the same proportions as in R_8S_1 (0.5 atmos. conc.), these would be:

Salt	*No. of increments*	*Volume molecular*
KH_2PO_4	8	.0082
$Ca(NO_3)_2$	1	.00075
$MgSO_4$	1	.0014

In combining these ratios, one for the cations and the other for the anions, it at once becomes apparent that the three salts considered would supply 5 parts too few of $H_2PO_4^-$, 2 parts too many of NO_3^-, and 3 parts too many of SO_4^{--} when the desired cation relationships were attained. To obviate this, some of the Ca^{++} and Mg^{++} must be supplied as $H_2PO_4^-$. A solution of the following composition would, therefore, contain cations as in R_3C_3 and anions as in R_8C_1:

Salt	*No. of increments*	*Volume molecular*
KH_2PO_4	3	.0031
$Ca(NO_3)_2$	1	.00075
$MgSO_4$	1	.0014
$CaH_4(PO_4)_2$	2	.0015
$MgH_4(PO_4)_2$	3	.0043

It should be emphasized, however, that the part of the total concentration due to cations is divided into tenths, as are the salts of Shive's triangle, and that

TABLE 1

Partial volume-molecular concentrations of salts in culture solutions at total concentrations of approximately 0.5 atmosphere possible osmotic pressure

SOLUTION NUMBERS	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$Ca(H_2PO_4)_2$	$Mg(H_2PO_4)_2$	KNO_3	$Mg(NO_3)_2$	K_2SO_4	$CaSO_4$
1. R_3C_3	.0031	.00225	.0057						
Cations as in R_3C_3									
2. Anions as in R_3C_1	.0031	.00075	.0014	.0015	.0043				
Cations as in R_3C_3									
3. Anions as in R_1C_3	.0010	.00225	.0014			.0021	.0043		
Cations as in R_3C_3									
4. Anions as in R_1C_1	.0010	.00075	.0057					.0021	.0015
Cations as in R_1C_3									
5. Anions as in R_1C_3	.0010	.0060	.0014						
Cations as in R_1C_3									
6. Anions as in R_3C_3	.0010	.00225	.0014	.0015					.0015
Cations as in R_1C_3									
7. Anions as in R_1C_1	.0010	.00075	.0014						.00525
Cations as in R_1C_3									
8. Anions as in R_3C_1	.0010	.00075	.0014	.00525					
Cations as in R_3C_1									
9. Anions as in R_3C_1	.0082	.00075	.0014						
Cations as in R_3C_1									
10. Anions as in R_3C_3	.0031	.00075	.0014			.0021		.0021	
Cations as in R_3C_1									
11. Anions as in R_1C_3	.0010	.00075	.0014			.0072			
Cations as in R_3C_1									
12. Anions as in R_1C_1	.0010	.00075	.0014					.0072	
Cations as in R_1C_1									
13. Anions as in R_1C_1	.0010	.00075	.0112						
Cations as in R_1C_1									
14. Anions as in R_3C_3	.0010	.00075	.0042		.0043		.0043		
Cations as in R_1C_1									
15. Anions as in R_1C_3	.0010	.00075	.0014				.0098		
Cations as in R_1C_1									
16. Anions as in R_3C_1	.0010	.00075	.0014		.0098				

any one cation may be varied in relative concentration with the other two, as long as the total number of increments remains at ten. If it is decided that eight parts of the cation concentration is to be due to K^+, then the parts of both Mg^{++} and Ca^{++} must be one each; and if it is desired to utilize eight parts of the total concentration of the anions as NO_3^-, then the parts of $SO_4^=$ and $PO_4^=$ must be one each. This solution is treatment 11 of this series, and the quantities of the various salts used are listed in tables 1 and 2. Table 1 gives the partial volume-molecular composition of the various treatments, with a total solution concentration of approximately 0.5 atmosphere. Table 2 gives the number of milliliters of stock solution required for each liter of nutrient

TABLE 2

Stock solutions required to produce 1 liter of nutrient solution, with total osmotic concentration of 0.5 atmosphere

TREATMENT NUMBER	0.5 *M* KH_2PO_4	0.5 *M* $Ca(NO_3)_2$	0.5 *M* $MgSO_4$	0.05 *M* $CaH_4(PO_4)_2$	0.05 *M* $MgH_4(PO_4)_2$	0.5 *M* KNO_3	0.5 *M* $Mg(NO_3)_2$	0.5 *M* K_2SO_4	0.01 *M* $CaSO_4$
	cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	6.2	4.5	11.4						
2	6.2	1.5	2.8	30.0	86.0				
3	2.0	4.5	2.8			4.2	8.6		
4	2.0	1.5	11.4					4.2	150.0
5	2.0	12.0	2.8						
6	2.0	4.5	2.8	30.0					150.0
7	2.0	1.5	2.8						525.0
8	2.0	1.5	2.8	105.0					
9	16.4	1.5	2.8						
10	6.2	1.5	2.8			4.2		4.2	
11	2.0	1.5	2.8			14.4			
12	2.0	1.5	2.8					14.4	
13	2.0	1.5	22.4						
14	2.0	1.5	8.4		86.0		8.6		
15	2.0	1.5	2.8				19.6		
16	2.0	1.5	2.8		196.0				

solution. The minor elements, iron, boron, and manganese were added to all solutions at the rate of 0.5 p.p.m.

Finally, the literature dealing with culture solutions contains statements that the two ions of any salt may retain a certain affiliation with each other when in solution, an assumption which has been based on measurements of absorption rates. If such were indeed the case, this revised system of physiological balance is obviously unjustifiable. Comparatively recent physical chemical research, however, justifies the assumption that mixtures of ions in solution have no such bonds of affiliation. The Debye-Milner theory of strong electrolytes (2) points out that electrical bonds between ions in solution do

exist, and that each ion in the solution has its electrical potential which exerts an influence over a limited sphere. However, inter-ionic forces are not specific in respect to the attraction of any negatively charged ion to a particular positively charged ion. And since X-ray analyses of crystal structure of these electrolytes have convinced physical chemists that the ions of strong electrolytes are actually in the ionic state even in the crystal, then in solution surely no such specific bonds develop. The greater burden of evidence substantiates this view. For a complete discussion of the physical properties of ions of strong electrolytes, see *Electrolytes* by Falkenhagen (2).

APPLICATION OF THE EXPERIMENTAL SYSTEM

Seed of the 1934 crop of Dave Croshaw's strain of Reed's yellow dent corn was furnished for the experiment by Dr. H. B. Sprague of the Agronomy Department of the New Jersey Agricultural Experiment Station. Only seeds selected for uniformity in size, weight, and shape of kernel were used. These were sown on April 20, 1935, in washed, white quartz sand, in 3-gallon glazed earthenware percolators. Twelve seeds, uniformly distributed, were sown in each percolator. Four uniform seedlings were selected from each percolator, and the others were removed by flooding the percolator with water and withdrawing the plants. In this way, the entire root system is easily removed, so that a minimum of organic material is left in the sand.

Sixty percolators of seedlings were started, and the forty-eight most uniform were selected for the experiment. This permitted three replications of each of the sixteen treatments. Solutions were first applied 9 days from planting and continued for 40 days, when the plants were harvested. Tap water was used to germinate the seeds.

Each culture received 2 liters of solution a day, one applied by the constant drip method, and the other in one application in the morning to flush the old solution from the sand.

During the course of growth, notes on differences were taken as they appeared. The plants were photographed 2 weeks before harvest, at which time the treatments high in Mg^{++} were showing rather severe toxicity symptoms. The younger leaves were tightly curled, and the edges of the blades were cracked and distorted. At the time of harvest, however, the plants had partially recovered from this injury without recourse to a change in treatment.

At the harvest, the plants were cut off just above the first visible node. Total green weight per plant was determined, and the leaves and stems were separated for analysis. The stem fraction included the stem, the leaf sheaths, and all tissue below the uppermost visible junction between leaf and leaf sheath.

These fractions of all the plants from each treatment were then diced and thoroughly mixed, and aliquots were weighed out for the various determinations. Dry weights were determined on duplicate aliquots. The samples were dried to constant weight at a temperature of 70–75°C.

PRESENTATION OF DATA

With such large differences between the solutions applied, it is to be expected that growth variations would be relatively extreme. Plates 1 and 2 give a visual conception of growth differences, which are presented in terms of green weight per plant in tables 3 and 4. The plants are arranged in subseries order, according to the ion present in high concentration. By inspection, the gross effect of the relative concentrations of the other ions present may be compared.

The data from the dry weight determinations are included in tables 5 and 6.

TABLE 3

Yields from the various treatments, arranged in subseries for comparison of anion effect upon growth

SUB-SERIES NUMBER	TREAT-MENT NUMBER	CATION PROPORTIONS			ANION PROPORTIONS			RANK	AVERAGE FRESH WEIGHT PER PLANT	AVERAGE DRY WEIGHT PER PLANT
		Ca^{++}	Mg^{++}	K^{+}	NO_3^{-}	$SO_4^{=}$	$PO_4^{\equiv}$			
									gm.	*gm.*
1	1	3	4	3	3	4	3	**	310 ± 11.8	26.36
	2	3	4	3	1	1	8		172 ± 7.6	15.76
	3	3	4	3	8	1	1	***	407 ± 24.5	34.60
	4	3	4	3	1	8	1	*	175 ± 3.6	15.95
2	5	8	1	1	8	1	1	***	297 ± 15.2	26.45
	6	8	1	1	3	4	3	**	269 ± 4.2	26.08
	7	8	1	1	1	8	1	*	161 ± 2.3	17.70
	8	8	1	1	1	1	8		130 ± 4.7	14.11
3	9	1	1	8	1	1	8		150 ± 2.9	15.02
	10	1	1	8	3	4	3	**	277 ± 14.7	24.20
	11	1	1	8	8	1	1	***	428 ± 14.1	32.59
	12	1	1	8	1	8	1	*	159 ± 2.9	15.88
4	13	1	8	1	1	8	1		112 ± 7.3	11.74
	14	1	8	1	3	4	3	**	158 ± 12.1	12.39
	15	1	8	1	8	1	1	***	173 ± 5.9	16.70
	16	1	8	1	1	1	8	*	129 ± 8.0	13.85

*** Signifies highest yielding treatment in subseries.
** Signifies 2nd highest yielding treatment in subseries.
* Signifies 3rd highest yielding treatment in subseries.

The per cent dry weight per plant is a calculated value, inasmuch as the actual per cent dry weight determinations were based on the stem and leaf fractions of the tissue. Individual weighings of the fresh leaf and stem fractions were taken at harvest, and the dry weight per plant was calculated from this and from the per cent dry weight of leaves and stems.

ANALYSIS OF DATA AND DISCUSSION OF RESULTS

The solutions in each of the subseries 1 to 4 are characterized by fixed cation proportions. Thus, in table 3, the different anion proportions for each sub-

series may be compared as they affect the yield in grams of green weight. It will be noted that for each of the four fixed cation proportions, the treatments high in NO_3^- and low in $PO_4^{\equiv}$ and $SO_4^{=}$ gave greater yields than did any other treatment. The anion proportions referred to R_3C_3 ranked second in each case, and the 1–8–1 porportions, high in $SO_4^{=}$, ranked third, except in subseries 4. The differences between the high $SO_4^{=}$ and high $PO_4^{\equiv}$ treatments are negligible in comparison to the other differences. The differences in yield associated with variations in anion proportions for given cation propor-

TABLE 4

Yields from the various treatments, arranged in subseries for comparison of cation effect upon growth

SUB-SERIES NUMBER	TREATMENT NUMBER	CATION PROPORTIONS			ANION PROPORTIONS			RANK	AVERAGE FRESH WEIGHT PER PLANT	AVERAGE DRY WEIGHT PER PLANT
		Ca^{++}	Mg^{++}	K^+	NO_3^-	SO_4^-	$PO_4^{\equiv}$			
									gm.	*gm.*
5	1	3	4	3	3	4	3	***	310 ± 11.8	26.36
	6	8	1	1	3	4	3	*	269 ± 4.2	26.06
	10	1	1	8	3	4	3	**	277 ± 14.7	24.20
	14	1	8	1	3	4	3		158 ± 12.1	12.39
6	2	3	4	3	1	1	8	***	172 ± 7.6	15.76
	8	8	1	1	1	1	8	*	130 ± 4.7	14.11
	9	1	1	8	1	1	8	**	150 ± 2.9	15.02
	16	1	8	1	1	1	8		129 ± 8.0	13.85
7	3	3	4	3	8	1	1	**	407 ± 24.5	34.60
	5	8	1	1	8	1	1	*	297 ± 15.2	26.45
	11	1	1	8	8	1	1	***	428 ± 14.1	32.59
	15	1	8	1	8	1	1		173 ± 5.9	16.70
8	4	3	4	3	1	8	1	***	175 ± 3.6	15.95
	7	8	1	1	1	8	1	**	161 ± 2.3	17.70
	12	1	1	8	1	8	1	*	159 ± 2.9	15.88
	13	1	8	1	1	8	1		112 ± 7.3	11.74

*** Signifies highest yielding treatment in subseries.

** Signifies 2nd highest yielding treatment in subseries.

* Signifies 3rd highest yielding treatment in subseries.

tions were greatest when the cation proportions were high in K^+, and least when they were high in Mg^{++}.

Hence, such comparisons show that the relative NO_3^- concentration is the limiting anion for the growth of corn under the conditions of this experiment, a conclusion previously reached by several workers; and also, that effectiveness of nitrate variation in producing changes in growth depends upon the attending proportion of the positively charged ions. It is evident that the NO_3^- is limiting even in the R_3C_3 concentration, and that this very pronounced importance of the NO_3^- completely overshadows the effect of the other two anions.

TABLE 5

Yield data for plants grown in culture solutions, grouped to determine the effect of anions upon growth

SUB-SERIES NUMBER	TREATMENT NUMBER	CATION PROPORTIONS	ANION PROPORTIONS	AVERAGE FRESH WEIGHT PER PLANT	AVERAGE DRY WEIGHT PER PLANT	PER CENT DRY WEIGHT PER PLANT	PER CENT DRY WEIGHT STEMS	PER CENT DRY WEIGHT LEAVES	WATER PER GRAM DRY WEIGHT STEMS	WATER PER GRAM DRY WEIGHT LEAVES
				gm.	*gm.*				*gm.*	*gm.*
1	1	As in R_3C_3	As in R_3C_3	307.7	26.36	8.56	6.47	14.31	14.45	5.99
	2	As in R_3C_3	As in R_8C_1 (high $PO_4^{\equiv}$)	171.2	15.76	9.20	6.28	14.38	14.92	5.92
	3	As in R_3C_3	As in R_1C_8 (high NO_3^-)	407.3	34.60	8.49	5.76	14.03	16.48	6.12
	4	As in R_3C_3	As in R_1C_1 (high $SO_4^{=}$)	175.1	15.95	9.11	6.28	14.59	14.92	5.86
2	5	As in R_1C_8 (high Ca^{++})	As in R_1C_8 (high NO_3^-)	295.6	26.45	8.95	5.76	14.70	16.36	5.80
	6	As in R_1C_8 (high Ca^{++})	As in R_4C_3	260.6	26.08	10.00	6.92	15.47	13.45	5.46
	7	As in R_1C_8 (high Ca^{++})	As in R_1C_1 (high $SO_4^{=}$)	161.3	17.70	10.96	7.72	16.91	11.96	4.92
	8	As in R_1C_8 (high Ca^{++})	As in R_8C_1 (high $PO_4^{\equiv}$)	130.4	14.11	10.81	7.51	16.37	12.31	5.11
3	9	As in R_8C_1 (high K^+)	As in R_8C_1 (high $PO_4^{\equiv}$)	149.5	15.02	10.04	6.64	14.65	14.06	5.82
	10	As in R_8C_1 (high K^+)	As in R_3C_3	275.1	24.20	8.80	6.08	14.35	15.45	5.97
	11	As in R_8C_1 (high K^+)	As in R_1C_8 (high NO_3^-)	427.3	32.59	7.62	5.09	13.14	18.64	6.61
	12	As in R_8C_1 (high K^+)	As in R_1C_1 (high $SO_4^{=}$)	158.7	15.88	10.00	6.98	15.44	13.33	5.48
4	13	As in R_1C_1 (high Mg^{++})	As in R_1C_1 (high $SO_4^{=}$)	112.5	11.74	10.44	7.53	15.27	12.28	5.54
	14	As in R_1C_1 (high Mg^{++})	As in R_3C_3	146.7	12.39	8.45	5.71	12.96	16.51	6.72
	15	As in R_1C_1 (high Mg^{++})	As in R_1C_8 (high NO_3^-)	164.3	16.70	10.15	6.18	13.76	15.18	6.26
	16	As in R_1C_1 (high Mg^{++})	As in R_8C_1 (high $PO_4^{\equiv}$)	129.1	13.85	10.75	7.68	15.95	12.02	5.27

TABLE 6

Yield data for plants grown in culture solutions, grouped to determine the effect of cations on growth

SUB-SERIES NUMBER	TREATMENT NUMBER	CATION PROPORTIONS	ANION PROPORTIONS	AVERAGE FRESH WEIGHT PER PLANT	AVERAGE DRY WEIGHT PER PLANT	PER CENT DRY WEIGHT PER PLANT	PER CENT DRY WEIGHT STEMS	PER CENT DRY WEIGHT LEAVES	WATER PER GRAM DRY WEIGHT STEMS	WATER PER GRAM DRY WEIGHT LEAVES
				gm.	*gm.*				*gm.*	*gm.*
5	1	As in R_3C_3	As in R_3C_3	307.7	26.36	8.58	6.47	14.31	14.45	5.99
	6	As in R_1C_8 (high Ca^{++})	As in R_3C_3	260.6	26.08	10.00	6.92	15.47	13.45	5.46
	10	As in R_8C_1 (high K^+)	As in R_3C_3	275.1	24.20	8.80	6.08	14.35	15.45	5.97
	14	As in R_1C_1 (high Mg^{++})	As in R_3C_3	146.7	12.39	8.45	5.71	12.96	16.51	6.72
6	2	As in R_3C_3	As in R_8C_1 (high $PO_4^{\equiv}$)	171.2	15.76	9.20	6.28	14.38	14.92	5.92
	8	As in R_1C_8 (high Ca^{++})	As in R_8C_1 (high $PO_4^{\equiv}$)	130.4	14.11	10.81	7.51	16.37	12.31	5.11
	9	As in R_8C_1 (high K^+)	As in R_8C_1 (high $PO_4^{\equiv}$)	149.5	15.02	10.04	6.64	14.65	14.06	5.82
	16	As in R_1C_1 (high Mg^{++})	As in R_8C_1 (high $PO_4^{\equiv}$)	129.1	13.85	10.73	7.68	15.95	12.02	5.27
7	3	As in R_3C_3	As in R_1C_8 (high NO_3^-)	407.3	34.60	8.49	5.76	14.03	16.48	6.12
	5	As in R_1C_8 (high Ca^{++})	As in R_1C_8 (high NO_3^-)	295.6	26.45	8.95	5.76	14.70	16.36	5.80
	11	As in R_8C_1 (high K^+)	As in R_1C_8 (high NO_3^-)	427.3	32.59	7.62	5.09	13.14	18.64	6.61
	15	As in R_1C_1 (high Mg^{++})	As in R_1C_8 (high NO_3^-)	164.3	16.70	10.15	6.18	13.76	15.18	6.26
8	4	As in R_3C_3	As in R_1C_1 (high $SO_4^=$)	175.1	15.95	9.11	6.28	14.59	14.92	5.86
	7	As in R_1C_8 (high Ca^{++})	As in R_1C_1 (high $SO_4^=$)	161.3	17.70	10.96	7.72	16.91	11.96	4.92
	12	As in R_8C_1 (high K^+)	As in R_1C_1 (high $SO_4^=$)	158.7	15.88	10.00	6.98	15.44	13.33	5.48
	13	As in R_1C_1 (high Mg^{++})	As in R_1C_1 (high $SO_4^=$)	112.5	11.74	10.44	7.53	15.27	12.28	5.54

The arrangement of treatments in table 4 allows for a similar inspection of the data on the cations. Thus, the R_3C_3 ratio of cation distribution shows the highest yield in all but subseries 7, in which the mean deviation in yields statistically nullifies the significance. The comparisons here are a bit irregular, but in general, high K^+ concentration is associated with slightly higher yields than is high Ca^{++}, which in turn is definitely superior to high Mg^{++} concentration. It is evident that cation variations are associated with the most pronounced growth variations when the anion distribution shows a high proportion of nitrate; and, conversely, cation variations are associated with least growth variation when nitrate supply is low and either phosphate or sulfate high. Of the cations, then, it appears that relatively larger proportions of K^+ and Ca^{++} are required than of Mg^{++}, in order to approach optimal growth.

Such an analysis does not attempt to show the actual relative contribution of each ion to the growth of the plant. It must be remembered, also, that these growth differences found may be due to deficiency or toxicity effects, and neither of these are clarified in this type of analysis. In all probability, furthermore, cation relationships are further complicated by antagonistic effects. The statistical analysis should allow for these factors.

STATISTICAL CONSIDERATION OF DATA

Justification for a statistical analysis lies in two facts: first, that each ion was applied in three definite relative proportions, one, three, and eight out of the total parts due to the ions carrying the common positive or negative charges; and, secondly, that each of these proportions was tested against a large number of individual plants.

In order to study the effect of the independent variables (the concentrations of the various ions) upon the dependent variable (growth as measured by grams green weight per plant), a multiple correlation analysis was employed. The fact that a purely mathematical analysis, in which the constants are determined by the method of least squares, entails such burdensome computations, led to the selection of the method of successive approximations as applied to curvilinear relationships (1). The regression equation upon which the computations were based is as follows:

$$X_1 = a' + f(X_2) + f(X_3) + f(X_4) + f(X_5) + f(X_6) + f(X_7)$$

In this equation, the dependent variable, X_1, is the average green weight of the plant; and of the independent variables, X_2 is the NO_3^-, X_3 the K^+, X_4 the $PO_4^{\equiv}$, X_5 the Ca^{++}, X_6 the $SO_4^{=}$, and X_7 the Mg^{++} concentration. The factor a' represents the effect on growth of all the factors, both genetic and environmental, which were held constant according to the conditions of the experiment. Briefly, this equation is a very general statement, in mathematical terms, that the growth of any selected plant is due to the influence of all environmental factors, which were the same for all plants, minimized genetic

differences, and some function of the influence of each of the ions which were varied in definite proportions, according to the conditions of the experiment.

The X' and Z' values, from which the part correlation indexes were determined, are presented in table 7. The X' terms represent the total statistical significance of the ion designated, in relation to growth in the various treatments. The Z' values are the unaccounted for residuals from the statistical analysis. The values plotted on the curves presented in figure 6 are derived from the X' values in the table. The curve that gives the yield corrected for NO_3^- represents the actual yield less that part of the yield due to the influence of the other five major ions; in other words, the constant a' is included in this curve. The zero abscissa of each of the other curves represents the NO_3^- curve

TABLE 7

Allowances and residuals from the statistical analysis

TREATMENT NUMBER	X_1	NO_3^-		K^+		$PO_4^{\equiv}$		Ca^{++}		$SO_4^=$		$Mg.^{++}$	
		X_2'	Z_2'	X_3'	Z_3'	X_4'	Z_4'	X_5'	Z_5'	X_6'	Z_6'	X_7'	Z_7'
1	307.7	253	10	47	10	1	10	−1	10	0	10	0	10
2	171.2	150	−20	47	−20	−3	−20	−1	−20	−1	−20	0	−20
3	407.3	326	34	47	34	2	34	−1	34	−1	34	0	34
4	175.1	150	−24	47	−24	2	−24	−1	−24	1	−24	0	−24
5	295.6	326	−33	−45	−29	2	−29	30	−24	−1	−24	8	−23
6	260.6	253	12	−45	16	1	16	30	21	0	21	8	22
7	161.3	150	5	−45	9	2	9	30	14	1	14	8	15
8	130.4	150	−19	−45	−15	−3	−15	30	−10	−1	−10	8	−9
9	149.5	150	−19	43	−28	−3	−28	−16	−30	−1	−30	8	−29
10	275.1	253	−2	43	−11	1	−11	−16	−13	0	−13	8	−12
11	427.3	326	76	43	67	2	67	−16	65	−1	65	8	66
12	158.7	150	−19	43	−28	2	−28	−16	−30	1	−30	8	−29
13	112.5	150	36	−45	40	2	40	−16	38	1	38	−16	36
14	146.7	253	−19	−45	−15	1	−15	−16	−17	0	−17	−16	−19
15	164.3	326	−77	−45	−73	2	−73	−16	−75	−1	−75	−16	−77
16	129.1	150	60	−45	64	−3	64	−16	62	−1	62	−16	60

straightened out so that any point on the curve can be represented as a zero value. The corrections for the other ions on total yield are either positive or negative with respect to this abscissa.

It must be remembered, in regard to these curves, that the total anion concentration is limited to ten relative parts. Therefore, if the hypothetical yield of any treatment is to be derived from the NO_3^- curve, the sum of the anion concentrations of the $SO_4^=$ and $PO_4^{\equiv}$ ions, plus the concentration of the NO_3^- ion at the point selected upon the upper curve, must total ten parts. Thus, if it is desired to compute the yield of a treatment with eight parts of NO_3^-, the correction on the NO_3^- curve for the effects of $PO_4^{\equiv}$ and $SO_4^=$ must be taken from the point on the curves corrected for each of these ions represented by one relative part. Any cation distribution may be arbitrarily se-

lected, as long as the total comes to ten relative parts, and these corrections are then added to the NO_3^- curve at the point previously selected.

The indexes of part correlation were computed in the standard manner (1).

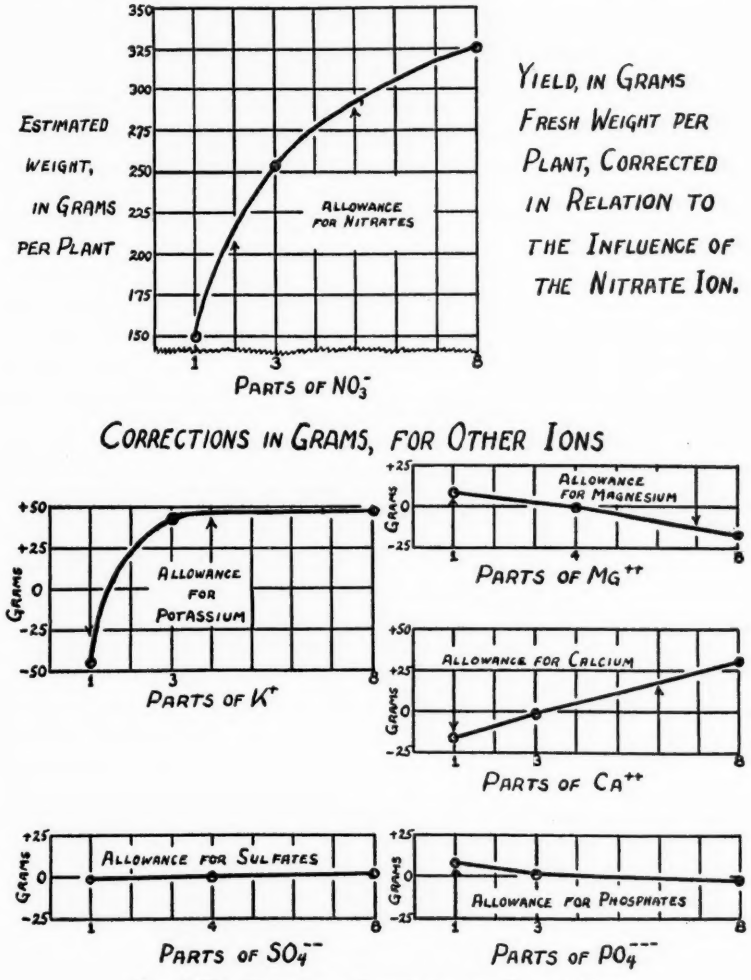

FIG. 6. NET REGRESSION CURVES FOR THE VARIOUS IONS

That is, if the net effect on growth due to a given ion is represented by D, and the difference between the observed yield and the summation of the net affects of all other ions except the one being considered is represented by Δ; then the coefficient of correlation between D and Δ ($r_{D\Delta}$) becomes the index of part cur-

vilinear correlation between growth and the given ion. These indexes as found for the various ions are presented in table 8.

These indexes, it should be recalled, show to what extent the variability indicated by the net regression curve of a given component accounts for the actual variability of this component. The indexes for NO_3^-, K^+, and Ca^{++} are indicative of a pronounced correlation between the concentration of these ions and plant growth. The highest of the correlations occurs between the nitrate supply and growth, with an index of part correlation of 0.874, with the indexes for K^+ and Ca^{++} 0.774 and 0.471 respectively. This, of course, means that the net regression curve for nitrate in figure 6 comes very close to being a true picture of the relationship between nitrate supply and growth when the effect of all other factors has been eliminated, inasmuch as an index of 0.874 indicates that practically all of the variability has been taken into account. Correspondingly, the curve for the net effect of K^+ concentration on growth represents the major portion of the growth variation associated with this ion. The curve for the net effect of calcium indicates the trend in growth variation accompanying variation in Ca^{++} concentration, but the index value of 0.471 shows that there are appreciable deviations which are not allowed for by this

TABLE 8

Indexes of part correlation

	NO_3^- 12·34567	$PO_4^{\equiv}$ 14·23567	$SO_4^{=}$ 16·23457	K^+ 13·24567	Ca^{+++} 15·23467	Mg^{++} 17·23456
Index of part correlation.....	.874	none	none	.774	.471	.224

curve. The net regression curve for magnesium has a negative slope, suggesting the tendency of increasing Mg^{++} concentration to become deleterious. The index value of 0.224 for the part correlation between Mg^{++} supply and growth indicates that there was considerable variation not represented by the regression curve. With reference to table 7, the high variation in the residuals of the high magnesium treatments, from -77 to $+60$, at once explains why such a low correlation index is found. Such high residual values indicate that consideration of the effect of each ion separately will not satisfactorily account for the yield variations observed but that a joint relationship between all or some of the ions is probably involved. Unquestionably there must be a direct relationship between the Mg^{++} and NO_3^- ionic concentrations which this analysis does not bring out.

The fact that no correlation is observed in the case of the anions $SO_4^{=}$ and $PO_4^{\equiv}$ with the growth of the plants, also evident in the horizontal net regression curves of figure 6, definitely establishes the fact that in no concentration used was there evidence of either deficiency or toxicity due to the concentrations of these ions. This fact simplifies a consideration of a possible joint functional relationship of growth to the relative concentrations of the four other ions; these four latter factors are, therefore, grouped together and con-

sidered as a joint factor influencing the growth of the plant. Since the $PO_4^{\equiv}$ and $SO_4^{=}$ concentrations have no effect upon growth, within the limits of this experiment, they may be excluded from the study of this joint functional relationship. Figure 7 is a graphic representation of this relationship, and the modified regression equation becomes:

$$X_1 = a' + f(X_4) + f(X_6) + f[X_2, X_3, X_5, X_7]$$

In each of the three diagrams of figure 7, the growth at a definite NO_3^- supply is plotted against the relative cation concentration. The base of each prism represents the triangle as used by Shive, but with the anions omitted;

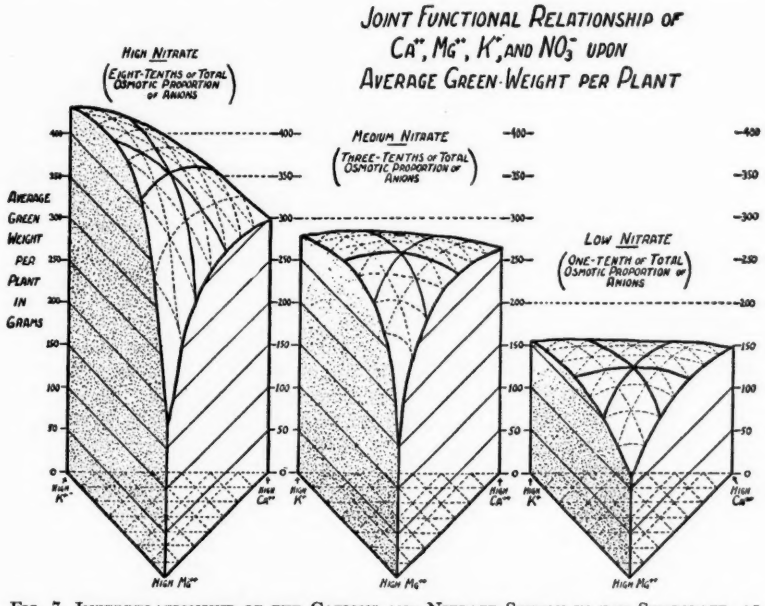
JOINT FUNCTIONAL RELATIONSHIP OF Ca++, Mg++, K+, AND NO3- UPON AVERAGE GREEN WEIGHT PER PLANT
HIGH NITRATE (EIGHT-TENTHS OF TOTAL OSMOTIC PROPORTION OF ANIONS)
MEDIUM NITRATE (THREE-TENTHS OF TOTAL OSMOTIC PROPORTION OF ANIONS)
LOW NITRATE (ONE-TENTH OF TOTAL OSMOTIC PROPORTION OF ANIONS)
AVERAGE GREEN WEIGHT PER PLANT IN GRAMS
HIGH K+
HIGH Ca++
HIGH Mg++

FIG. 7. INTERRELATIONSHIP OF THE CATIONS AND NITRATE SUPPLY IN THE SUBSTRATE, AS THEY INFLUENCE GROWTH OF THE PLANT

consequently it is representative of the cation distribution only. Each prism, therefore, represents the effect of the cation distribution upon growth, at a definite NO_3^- level. The $PO_4^{\equiv}$ and $SO_4^{=}$ ions are completely omitted from consideration in this study, an omission justified by the facts that there was no calculable correlation between the relative concentrations of these ions and growth, and that the net regression curve for each of these ions was horizontal.

If in any of the prisms, therefore, there were no significant differences in terms of growth, due to the differences in the relative amounts of the cations supplied, the upper surface of that prism would be a duplication of the base. Also, if there were no correlation between the relative NO_3^- supply and the

relative cation distribution, the regression surface of all three prisms would be identical.

With this in mind, a comparison of the three prisms shows that the ability of the plant to utilize NO_3^- in increasingly high concentration is closely correlated with the cation distribution. The greater the distortion of the regularity of the triangular upper surface of the prism, the greater is the significance of the cation distribution. Therefore, if the NO_3^- is present in limited quantity, there is little significance in the cation distribution as this affects the growth of the plants. At the other extreme, with an abundance of NO_3^-, the ability of the plant to utilize this ion most efficiently is clearly limited by the relative cation distribution. In brief, then, the higher the supply of available NO_3^- in the substrate, the more important the relative cation distribution becomes. K^+ would appear to be necessary in greater concentration than Ca^{++}, under conditions of high available NO_3^-, and Mg^{++} seems necessary in much lesser amounts than either K^+ or Ca^{++}. On the other hand, the relatively flat upper regression surface of the prism which represents the plants grown at the low NO_3^- level suggests that here there can be little significance attached to the relative cation distribution. The toxicity symptoms observed in the high Mg^{++} treatments were correspondingly less significant at the low NO_3^- level.

This joint functional relationship suggests that a profitable means of study of cation balance in the substrate would be through a study of the nitrogen assimilation, as shown by the nitrogen fractions found in tissue analyses.

This type of consideration of the cations would indicate that cation ratios, as considered previously by other investigators, are not inclusive enough, and that any consideration of the cation supply must include the relative concentration of all three cations to have full significance. None of the three ratios, Ca/Mg, K/Mg, or K/Ca, shows any significance in this series.

Table 7 includes the data of the dry weight determinations. It is evident here, too, that the nitrate supply is without question the factor which extends the greatest influence over the per cent of dry weight. In every treatment, both in the leaf and stem fractions, the number of grams of water per gram dry weight increases with increased NO_3^- in the nutrient medium. Probably stored carbohydrates in the low NO_3^- plants accounts for this in part, at least. This is in direct agreement with the bulk of accumulated data.

The treatments high in K^+ in the nutrient solution all produced tissue higher in water content than those grown with high Ca^{++}. The necessity of soluble potassium at the rapidly growing regions is probably a factor here.

The treatments high in Ca^{++} were consistently higher in per cent dry weight than were any of the other treatments. Probably the factors which cause this condition are very complex, and may be demonstrable in the chemical or morphological analyses of the tissues.

The data from the high Mg^{++} treatments do not allow satisfactory conclusions to be drawn with regard to the effect of this cation upon per cent dry weight. The general statement holds true that the treatments which produced

plants of high average green weight also produced plant tissue of a low percentage of dry weight, with the exception of those treatments high in Mg^{++}, which were irregular in this respect.

The fact should be emphasized that only four of the solutions of Shive's triangle have been dealt with in these experiments. The triangle, represents 36 different solutions, any of which might be used in similar experiments. A selection of several of the solutions which customarily produce high yields, and a variation of the ionic concentrations in some regulated manner such as has been used in these experiments, may prove of considerable value in nutritional work.

SUMMARY AND ABSTRACT

A system of physiologically balanced solutions is presented in which it is possible to vary the concentration of any or all of the individual ions and to isolate the effect of any ion or combination of ions upon plant growth, as measured by average green weight per plant.

The series of solutions was used in the growth of a strain of hybrid corn, and the growth of the plants was used as a means of comparison of the effects of the ions.

A statistical analysis was employed with the data obtained, and the following conclusions were drawn from a consideration of the indexes of part correlation and of the net regression curves:

No correlation was observed between the amounts of $SO_4^{=}$ or $PO_4^{\equiv}$ in the substrate and the growth of the plants within the limits of the concentrations employed.

Increasingly high concentrations of NO_3^- in the substrate, between the limits of one and eight out of a total of ten relative parts of the anion concentration, gave the most marked correlations with increases in growth.

Increasingly high concentrations of both K^+ and Ca^{++}, between the same concentration limits, gave marked increases in growth.

Increasingly high concentrations of Mg^{++}, between the same limits, resulted in decreased growth, producing symptoms of toxicity in the high concentration utilized. The net regression curve had a negative slope within the limits of the variation of the Mg^{++} supply in the substrate.

The importance of the relative concentrations of the cations is entirely dependent upon the amount of NO_3^- present in the substrate. At low concentrations of NO_3^- little importance can be attached to the relative proportions of the three cations. At higher concentrations of NO_3^-, the necessity for higher relative proportions of K^+ and Ca^{++} and for lower relative proportions of Mg^{++} in the substrate for maximum response to the NO_3^-, is brought out. With high concentrations of both Mg^{++} and NO_3^-, the toxicity of the Mg^{++} is particularly noticeable in the manner in which it inhibits the growth of the plants.

None of the three cation ratios, Ca/Mg, K/Mg, or K/Ca, show any significance in these experiments.

The dry weight data showed correlations between the percentage of dry

weight and relative concentrations of three of the major nutritional elements. The higher the available relative amounts of both NO_3^- and K^+, the lower the percentage of dry weight of the tissues produced. With increasing Ca^{++} concentration in the medium, there was a higher percentage of dry material in the tissues.

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PLATE 1

PLANTS FROM THE VARIOUS TREATMENTS ARRANGED IN SUBSERIES FOR COMPARISON OF ANION EFFECTS UPON GROWTH

The numbers at the base of the cultures correspond to the treatment numbers given in table 3.

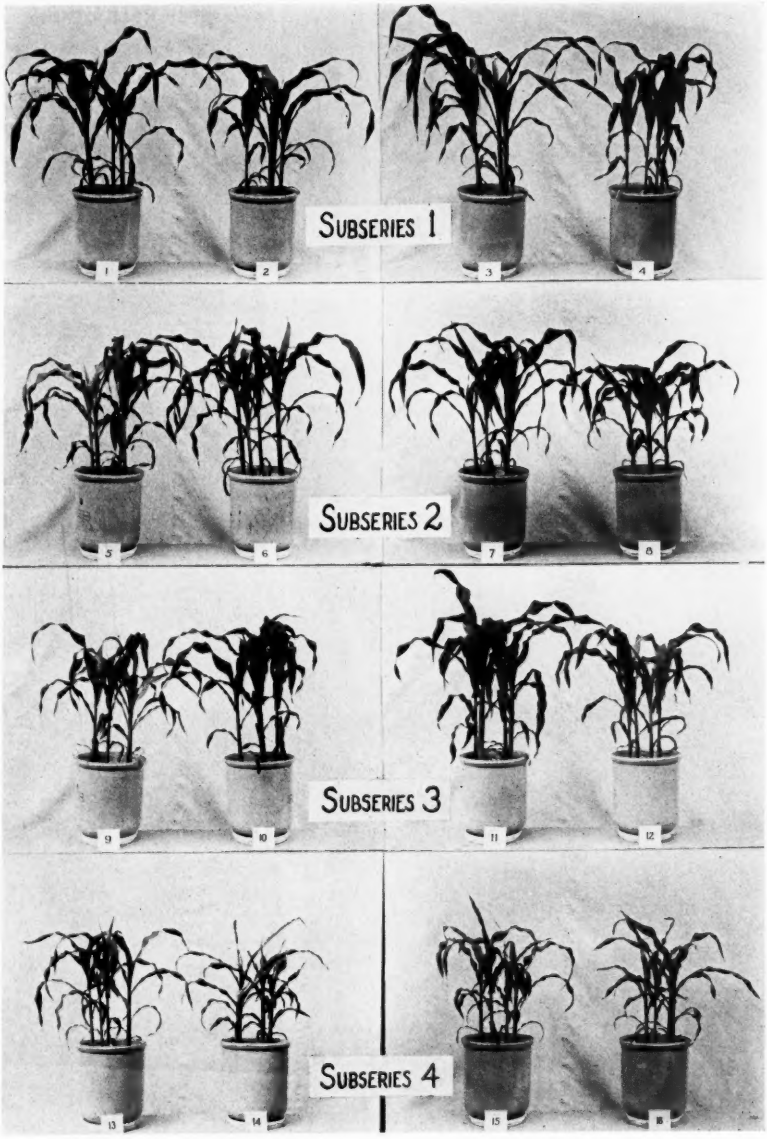
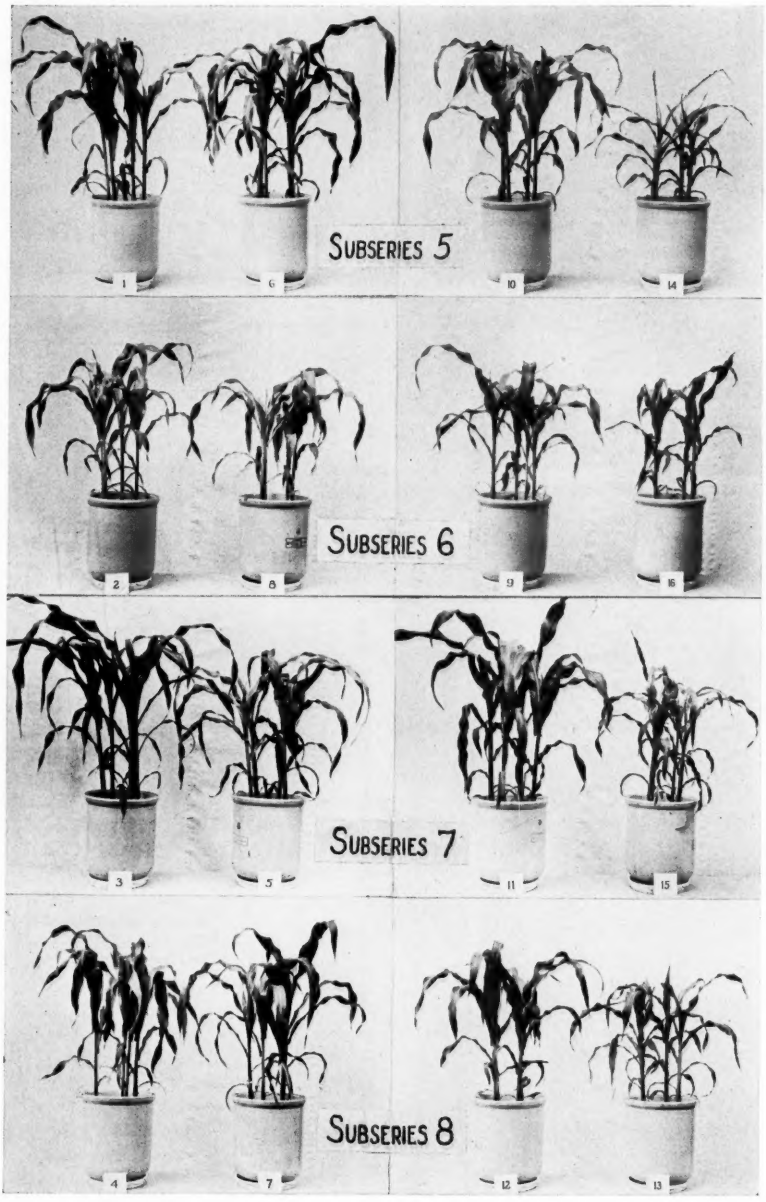

SUBSERIES 1
SUBSERIES 2
SUBSERIES 3
SUBSERIES 4

PLATE 2

PLANTS FROM THE VARIOUS TREATMENTS ARRANGED IN SUBSERIES FOR COMPARISON OF CATION EFFECT UPON GROWTH

The numbers at the base of the cultures correspond to the treatment numbers given in table 4.



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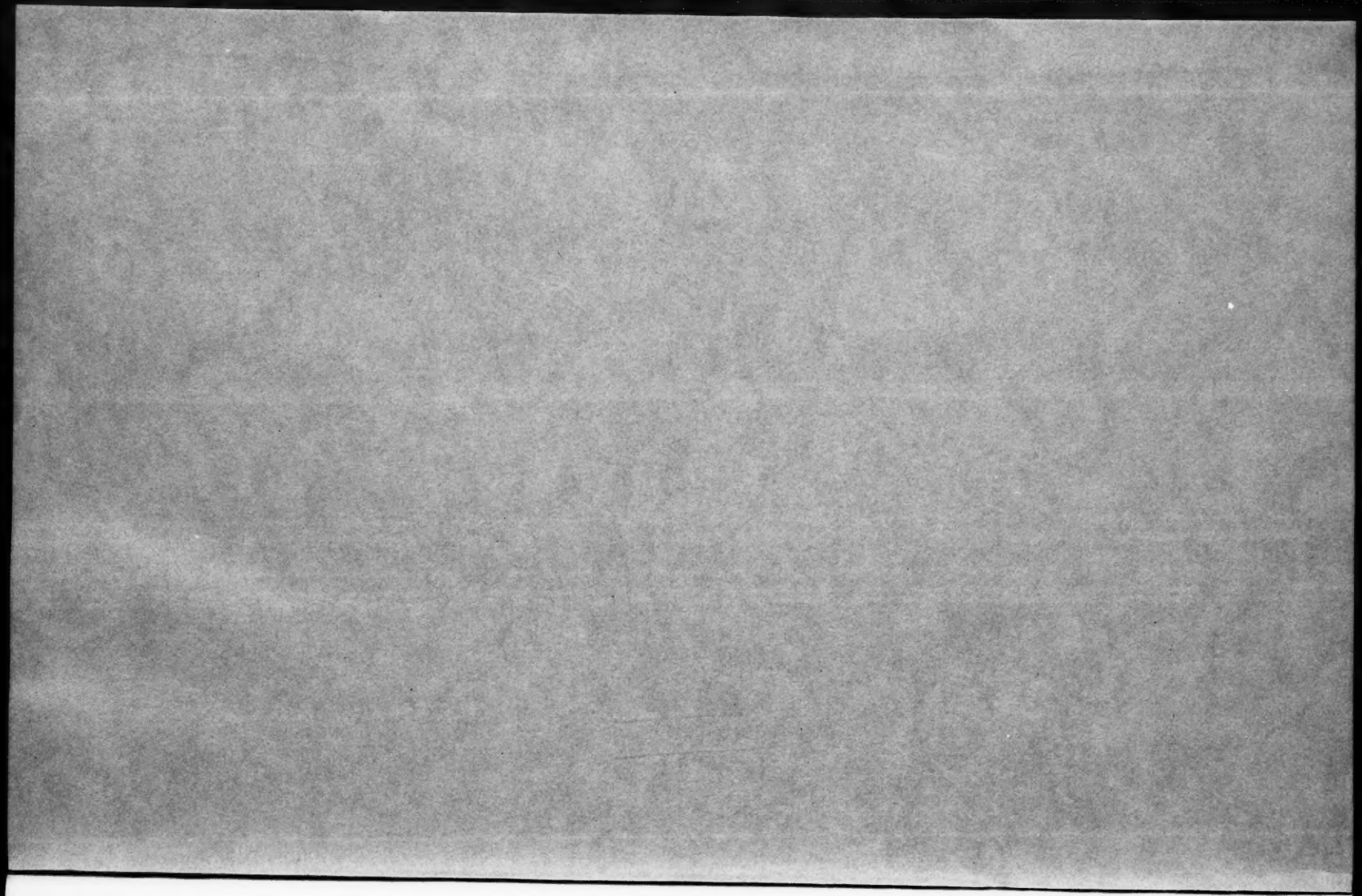
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